1973

Some Studies In Intermolecular Forces

Yuh-hsu Pan

Follow this and additional works at: https://ir.lib.uwo.ca/digitizedtheses

Recommended Citation

Pan, Yuh-hsu, "Some Studies In Intermolecular Forces" (1973). Digitized Theses. 735.
https://ir.lib.uwo.ca/digitizedtheses/735
The author of this thesis has granted The University of Western Ontario a non-exclusive license to reproduce and distribute copies of this thesis to users of Western Libraries. Copyright remains with the author.

Electronic theses and dissertations available in The University of Western Ontario’s institutional repository (Scholarship@Western) are solely for the purpose of private study and research. They may not be copied or reproduced, except as permitted by copyright laws, without written authority of the copyright owner. Any commercial use or publication is strictly prohibited.

The original copyright license attesting to these terms and signed by the author of this thesis may be found in the original print version of the thesis, held by Western Libraries.

The thesis approval page signed by the examining committee may also be found in the original print version of the thesis held in Western Libraries.

Please contact Western Libraries for further information:
E-mail: libadmin@uwo.ca
Telephone: (519) 661-2111 Ext. 84796
Web site: http://www.lib.uwo.ca/
SOME STUDIES IN INTERMOLECULAR FORCES

by

Yuh-Hsu Pan

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
March 1973

© Yuh-Hsu Pan 1973
ABSTRACT

Rayleigh-Schrödinger perturbation theory is used to investigate the dependence of the asymptotic divergent behaviour of the $R^{-1}$ series representations of long range intermolecular forces on the nature of the interacting species. The investigations are based on the Unsöld's approximation for the second order perturbation energy using He-He, $H(1s)-H^+$, $H(1s)-H(1s)$ and $H(1s)-H(2s)$ as models representing non-bonded and bonded or excited state interactions. The Padé approximation method is used to accelerate the convergence of the $R^{-1}$ series obtained from the above mentioned model calculations and to give a more realistic indication of the asymptotic nature of the series.

The generalized Brillouin-Wigner perturbation theory in the Unsöld's approximation is modified to avoid some computational difficulties in the original method. The usefulness of this modified perturbation technique for calculating intermediate and large range intermolecular forces, including charge overlap and exchange effects, is tested by calculations of interaction energies for the
$X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $C^1\Pi_u$, $^3\Pi_g$, $^1\Pi_g$ and $^3\Pi_u$ states of the $H_2$ molecule.

The usual (fixed) one centre method is briefly reviewed and its "misbehaviour" in calculating energies of diatomic molecules for intermediate and large internuclear separations is discussed. The fixed one centre method is generalized to one or two floating centres to calculate the energies of diatomic molecules for all $R$. The connection of this floating centre(s) method with the fixed one centre method and the long range treatment of intermolecular forces are also discussed. Finally the usefulness of the floating centre(s) approach is investigated by model energy calculations of the ground state $H_2^+$ and $H_2$ molecules.
ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor W.J. Meath for his invaluable advice, patient guidance and continued encouragement during the course of this work.

He also wishes to express his deep appreciation to his colleagues for their useful discussions and assistance in general. In particular, thanks are due to Mr. J.P. Bukta, Dr. H. Kreek and Dr. J.E. Kouba for their advice and assistance on computations.

The author is also indebted to Dr. H.D. Todd of Wesleyan University, Connecticut, U.S.A. for supplying the computer program "TWOCEM".

The financial support given by the Department of University Affairs of Ontario is gratefully acknowledged.

Many thanks are also extended to Mrs. Joyce Kilbourne for her accurate typing.

Finally the author wishes to thank his wife, Tao-Wan, for her understanding and patience.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. MODEL STUDY OF CHARGE OVERLAP EFFECTS IN INTERMOLECULAR FORCES VIA PERTURBATION THEORY</td>
<td>8</td>
</tr>
<tr>
<td>2.1 A Perturbation Theory Approach Neglecting Electron Exchange Effects</td>
<td>8</td>
</tr>
<tr>
<td>2.1A General Results</td>
<td>9</td>
</tr>
<tr>
<td>2.1B Non-resonant (Direct) Interactions</td>
<td>13</td>
</tr>
<tr>
<td>2.1C Resonant Interactions</td>
<td>14</td>
</tr>
<tr>
<td>2.1D Unsöld's Approximation</td>
<td>16</td>
</tr>
<tr>
<td>2.2 The Multipole Expansion and &quot;Long Range&quot; Interaction Energies</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Second Order Charge Overlap Effects in Unsöld's Approximation</td>
<td>23</td>
</tr>
<tr>
<td>2.3A The Non-expanded and Expanded Second Order Energies in Unsöld's Approximation for the H(1s)−H(2s) Interaction</td>
<td>24</td>
</tr>
<tr>
<td>2.3B Dependence of Second Order Charge Overlap Effects on the Nature of the Interaction Using Model Interactions as Examples</td>
<td>29</td>
</tr>
</tbody>
</table>
2.3C Second Order Charge Overlap Effects
Using the Exact Treatment of the
H(1s)-H⁺ Interaction .......................... 43

2.4 Padé Approximation Methods Applied to the
Intermolecular Force Series ...................... 46

2.4A Padé Approximants ......................... 47

2.4B Results and Discussions .................... 50

3. GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY
CAlCULATIONS OF INTERMOLECULAR FORCES INCLUDING
EXCHANGE EFFECTS ........................................ 61

3.1 Generalized Brillouin-Wigner Perturbation
Theory .................................................. 63

3.1A General Theory ............................... 63

3.1B Unsöld's Approximation for the Generalized
Brillouin-Wigner Perturbation Theory ............ 67

3.1C Modification of the Generalized
Brillouin-Wigner Perturbation Theory
in the Unsöld's Approximation ................. 69

3.2 Application of the Modified Brillouin-
Wigner Perturbation Theory in Unsöld's
Approximation to Intermolecular Forces ....... 71

3.3 Application of the Modified Unsöld's
Approximate Generalized Brillouin-Wigner
Perturbation Theory to Some H(1s)-H(n=2)
Interactions ............................................. 75

3.4 Results and Discussions .................... 85

4. FLOATING ONE AND TWO CENTRE CALCULATIONS OF
INTERMEDIATE AND LONG RANGE INTERMOLECULAR
FORCES .................................................. 97

4.1 Brief Review and Deficiencies of the Fixed
One Centre Method ................................... 98

4.1A Homonuclear Diatomic Molecules ........... 98
4.1B Heteronuclear Diatomic Molecules ........... 102
4.2 Modification of the Fixed One Centre Method ........................................ 105
4.2A Homonuclear Diatomic Molecules ........... 105
4.2B Heteronuclear Diatomic Molecules ........... 108
4.3 The Floating Centre(s) Method ............... 110
4.3A Perturbation Theory Approach ............... 111
4.3B Variational Method Approach ............... 120
4.4 Variational Floating Centre(s) Calculations for $H_2^+$ and $H_2$ .................... 121
4.4A Method of Calculation ........................ 123
4.4B Results and Discussion for $H(ls)-H_1^+$ .... 125
4.4C Results and Discussion for $H(ls)-H(ls)$ .. 140
4.5 General Discussion of the Convergence of the Floating Centre(s) Method for the Model Ground State $H(ls)-H_1^+$ and $H(ls)-H(ls)$ Interactions ........................................ 152
5. CONCLUSIONS ......................................................... 158

APPENDICES

A. The Separation of $E_{res}^{(2)}$ of Sec. 2.1C into Induction and Dispersion Energies ............... 162
B. The Mixing of $1s2s$ and $1s2p_\sigma$ Configurations for the $H(ls)-H(n=2)$ Interaction .................. 164
C. The Evaluation of the Non-Expanded Unsöld's Second Order Interaction Energies for the $H(ls)-H(2s)$ Interaction ........................................ 170

C.1 Discussion of the Evaluation of the Basic Integrals Defined in Sec. (C.2) .................. 170
C.2 Integral List for the Model Calculations of the $H(ls)-H(2s)$ Interaction of Sec. 2.3A ............... 171
C.3 Explicit Expressions for the Integrals
Listed in (C.2) ................................. 172

C.4 The Non-expanded Second Order Energies
in Unsöld’s Approximation for the
H(1s)—H(2s) Interaction of Sec. 2.3A ......... 174

D. The Evaluation of the Expanded Unsöld’s Second
Order Interaction Energies for the H(1s)—H(2s)
Interaction ........................................ 178

E. The Mixing of 1s2s and 1s2pσ Configurations,
Including Electron Exchange, for the a3Σ+ state
of H(1s)—H(n=2) Interaction ..................... 179

F. The Variational Procedure ........................ 182

REFERENCES ........................................... 184

VITA .................................................. 195
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.2-1)</td>
<td>Coordinate axes used for the computation of molecular interaction energies.</td>
<td>19</td>
</tr>
<tr>
<td>(2.3-1)</td>
<td>A comparison of the ratios, $\frac{E^{(2)}}{E^{(2)}}$, as a function of $R$ for the various interactions considered in Sec. 2.3.</td>
<td>36</td>
</tr>
<tr>
<td>(2.3-2)</td>
<td>A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s)$-$\text{H}^+$ interaction in Unsöld's approximation.</td>
<td>38</td>
</tr>
<tr>
<td>(2.3-3)</td>
<td>A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{He}$-$\text{He}$ interaction in Unsöld's approximation.</td>
<td>39</td>
</tr>
<tr>
<td>(2.3-4)</td>
<td>A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s)$-$\text{H}(1s)$ interaction in Unsöld's approximation.</td>
<td>40</td>
</tr>
<tr>
<td>(2.3-5)</td>
<td>A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s)$-$\text{H}(2s)$ interaction in Unsöld's approximation.</td>
<td>41</td>
</tr>
<tr>
<td>(2.3-6)</td>
<td>A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s)$-$\text{H}^+$ interaction using exact results.</td>
<td>45</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>(2.4-1)</td>
<td>A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)-H⁷⁺ interaction in Unsöld's approximation.</td>
<td>52</td>
</tr>
<tr>
<td>(2.4-2)</td>
<td>A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of R for the He-He interaction in Unsöld's approximation.</td>
<td>53</td>
</tr>
<tr>
<td>(2.4-3)</td>
<td>A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)-H(1s) interaction in Unsöld's approximation.</td>
<td>54</td>
</tr>
<tr>
<td>(2.4-4)</td>
<td>A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)-H(2s) interaction in Unsöld's approximation.</td>
<td>55</td>
</tr>
<tr>
<td>(2.4-5)</td>
<td>A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)-H⁺ interaction using exact results.</td>
<td>57</td>
</tr>
<tr>
<td>(4.1-1)</td>
<td>Comparison of the interaction energy calculated from the fixed internuclear mid-point one centre method using the basis set {1s,2s} with the corresponding exact results for ground state H₂⁺ as a function of R.</td>
<td>103</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>(4.1-2)</td>
<td>Comparison of the interaction energy calculated from the fixed internuclear midpoint one centre method using the basis set (1s^2, 2p^2) with the corresponding exact results for ground state (H_2) as a function of (R).</td>
<td>104</td>
</tr>
<tr>
<td>(4.2-1)</td>
<td>Comparison of the interaction energy calculated from the floating one centre method using the basis set (1s, 2s) with the corresponding exact results for ground state (H_2^+) as a function of (R).</td>
<td>107</td>
</tr>
<tr>
<td>(4.2-2)</td>
<td>Comparison of the interaction energy calculated from the floating two centre method using the basis set (1s^2, 2p^2) with the corresponding exact results for ground state (H_2) as a function of (R).</td>
<td>109</td>
</tr>
<tr>
<td>(4.3-1)</td>
<td>Coordinate system for the floating centre(s) method.</td>
<td>114</td>
</tr>
<tr>
<td>(4.4-1)</td>
<td>Comparison of the interaction energy calculated from the floating one centre method, using various basis sets, with the corresponding exact results for ground state (H_2^+) as a function of (R).</td>
<td>127</td>
</tr>
<tr>
<td>(4.4-2)</td>
<td>Optimal values of the floating parameter (\rho), for various basis sets, as a function of (R) for ground state (H_2^+).</td>
<td>135</td>
</tr>
<tr>
<td>(4.4-3)</td>
<td>Comparison of the interaction energy obtained from the basis sets (1s, 2s, 2p) and (1s, 2s, 2p, 3d, 4f, 5g, 6h, 7i), for various choices of the expansion centre, with the corresponding exact results for ground state (H_2^+) as a function of (R).</td>
<td>136</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>(4.4-4)</td>
<td>Comparison of the interaction energy calculated from the floating two centre method, using various basis sets, with the corresponding exact results for ground state H₂ as a function of R.</td>
<td>147</td>
</tr>
<tr>
<td>(4.4-5)</td>
<td>Comparison of the interaction energy obtained from the basis sets {1s^2,2p^2} and {1s^2,2p^2,3p3d,3d^2,2p4f,3d4f,4f^2}, for various choices of expansion centres, with the exact results for ground state H₂ as a function of R.</td>
<td>149</td>
</tr>
<tr>
<td>(4.4-6)</td>
<td>Comparison of the interaction energy obtained from the basis sets {1s^2,1s2p,2p^2} and {1s^2,1s2p,2p^2,3p3d,3d^2,2p4f,3d4f,4f^2}, for various choices of expansion centres, with the exact results for ground state H₂ as a function of R.</td>
<td>151</td>
</tr>
<tr>
<td>(F.1)</td>
<td>Flow diagram for the &quot;Pattern Search&quot; method used to find the minimum energies for the H₂⁺ and H₂ molecules.</td>
<td>183</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.3-1)</td>
<td>Second order energies in units of the Unsöld's average energy $\Delta$ for the $H(1s)$-$H(2s)$ interaction as a function of $R$.</td>
<td>28</td>
</tr>
<tr>
<td>(2.3-2)</td>
<td>Comparison of the resonant Unsöld's expansion coefficient, Eq. (2.3-11), with the direct Unsöld's expansion coefficient, Eq. (2.3-10), as a function of $m$.</td>
<td>30</td>
</tr>
<tr>
<td>(2.3-3)</td>
<td>Ratios of the coefficients of successive terms in the $R^{-1}$ expansion of some second-order dispersion energies.</td>
<td>33</td>
</tr>
<tr>
<td>(2.4-1)</td>
<td>Values of $p_i$ and $q_i$ of Eq. (2.4-3), $i \geq 1$, given in terms of the coefficients of the power series, $\sum_{n=0}^\infty \tilde{C}_2^{(2)}(n+k) x^n$, for various Padé approximants.</td>
<td>49</td>
</tr>
<tr>
<td>(2.4-2)</td>
<td>Results of summing $R^{-1}$ series in Unsöld's approximation, by the method of Dalgarno and Lewis, for various interactions.</td>
<td>59</td>
</tr>
<tr>
<td>(3.3-1)</td>
<td>Values for the parameters, $\eta$ and $\rho$, used to specify the wavefunction, Eq. (3.3-1), for various molecular states of $H_2$ considered in Sec. 3.3.</td>
<td>78</td>
</tr>
<tr>
<td>(3.3-2)</td>
<td>Values for the &quot;exact&quot; Unsöld's expansion coefficients, $\tilde{C}_m^{(2)}$, $m = 6, 8$, in units of $\Delta^{-1}$, for various states of some $H(1s)$-$H(n \ell m)$ interactions.</td>
<td>81</td>
</tr>
<tr>
<td>(3.4-1)</td>
<td>A comparison of some total and Coulomb modified Unsöld's interaction energies through second order with the exact total and long range interaction energies for the $X^1\Sigma_g^+$ state of $H_2$ as a function of $R$.</td>
<td>86</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>(3.4-2)</td>
<td>A comparison of some total modified Unsöld's interaction energies through second order with the exact total interaction energy for the $b^3\Sigma_u^+$ state of $H_2$ as a function of $R$.</td>
<td>87</td>
</tr>
<tr>
<td>(3.4-3)</td>
<td>A comparison of some total and Coulomb modified Unsöld's interaction energies through second order with the exact total and long range interaction energies for the $a^3\Sigma_g^+$ state of $H_2$ as a function of $R$.</td>
<td>88</td>
</tr>
<tr>
<td>(3.4-4)</td>
<td>A comparison of some total and Coulomb modified Unsöld's interaction energies through second order with the exact total and long range interaction energies for the $c^1\Pi_u$ state of $H_2$ as a function of $R$.</td>
<td>89</td>
</tr>
<tr>
<td>(3.4-5)</td>
<td>A comparison of the total modified Unsöld's interaction energy through second order with Browne's total variational interaction energy for the $^3\Pi_g$ state of $H_2$ as a function of $R$.</td>
<td>92</td>
</tr>
<tr>
<td>(3.4-6)</td>
<td>A comparison of the total and Coulomb modified Unsöld's interaction energies through second order with Browne's total variational and long range interaction energies for the $^1\Pi_g$ state of $H_2$ as a function of $R$.</td>
<td>93</td>
</tr>
<tr>
<td>(3.4-7)</td>
<td>A comparison of the total modified Unsöld's interaction energy through second order with Browne's total variational interaction energy for the $^3\Pi_u$ state of $H_2$ as a function of $R$.</td>
<td>94</td>
</tr>
<tr>
<td>(3.4-8)</td>
<td>A comparison of the total modified Unsöld's interaction energy through second order with Kreek's &quot;exact&quot; Unsöld's interaction energy, $\mathcal{E}_{ab}$(Kreek), through second order for the $X^1\Sigma_g^+$ state of $H_2$ as a function of $R$.</td>
<td>96</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>(4.1-1)</td>
<td>Some fixed one centre results for the interaction energy, $E_{ab}$, of ground state $H_2^+$ and $H_2$ at their equilibrium separations.</td>
<td>100</td>
</tr>
<tr>
<td>(4.4-1)</td>
<td>Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of the basis set size for the H(1s)–H$^+$ interaction at $R = 6$ a$_0$.</td>
<td>128</td>
</tr>
<tr>
<td>(4.4-2)</td>
<td>Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of $l$ for the H(1s)–H$^+$ interaction at $R = 6$ a$_0$.</td>
<td>131</td>
</tr>
<tr>
<td>(4.4-3)</td>
<td>Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ calculated from basis sets containing a [1s] core and even or odd orbitals only as a function of $R$ for the H(1s)–H$^+$ interaction.</td>
<td>132</td>
</tr>
<tr>
<td>(4.4-4)</td>
<td>Optimum values for the floating parameter $\rho$ and screening constants $\eta$ and the interaction energy $\tilde{E}_{ab}$ as a function of $R$ when the basis set {1s,2s,2p,3d,4f,5g,6h,7i} is used in the variational calculations of the H(1s)–H$^+$ interaction.</td>
<td>138</td>
</tr>
<tr>
<td>(4.4-5)</td>
<td>Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of the basis size for the H(1s)–H(1s) interaction at $R = 6$ a$_0$.</td>
<td>142</td>
</tr>
<tr>
<td>(4.4-6)</td>
<td>Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of $l$ for the H(1s)–H(1s) interaction at $R = 4$ and 6 a$_0$.</td>
<td>144</td>
</tr>
<tr>
<td>(4.4-7)</td>
<td>Optimum values for the floating parameter $\rho$ and screening constants $\eta$ and the interaction energy $\tilde{E}_{ab}$ as a function of $R$ when the basis set {1s$^2$,1s2p,$^2$1p,$^2$1s3d,2p3d,3d$^2$,2p4f,3d4f,4f$^2$} is used in the variational calculations of the H(1s)–H(1s) interaction.</td>
<td>146</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>(4.5-1)</td>
<td>The interaction energies and the optimum values for the variational parameters in the basis sets {ns, n'p, n''d} and {ls^2, 2p^2, 10p^2} used for the calculations of ground state energies for H_2^+ and H_2 respectively at R = 6 , a_0.</td>
<td>157</td>
</tr>
<tr>
<td>(B.1)</td>
<td>(^1\Sigma^+_g\left(^3\Sigma^+<em>u\right)) states of H_2. First order energies and coefficients of mixing for the 1s2s and 1s2p</em>\sigma configurations.</td>
<td>167</td>
</tr>
<tr>
<td>(B.2)</td>
<td>(^1\Sigma_u\left(^3\Sigma_g^+\right)) states of H_2. First order energies and coefficients of mixing for the 1s2s and 1s2p_\sigma configurations.</td>
<td>168</td>
</tr>
<tr>
<td>(E.1)</td>
<td>(^3\Sigma_g^+) states of H_2. First order energies and coefficients of mixing for the 1s2s and 1s2p_\sigma configurations including electron exchange.</td>
<td>180</td>
</tr>
</tbody>
</table>
1. **INTRODUCTION**

The interaction energy between two molecules "a" and "b" is defined as

\[ E_{ab} = E - E^{(o)} \]  \hspace{1cm} (1.1-1)

where \( E \) is the energy of the total system obtained by solving the Schrödinger equation for the two interacting molecules,

\[ H \Psi = E \Psi \]  \hspace{1cm} (1.1-2)

and \( E^{(o)} \) is the energy of the isolated molecules obtained by solving the Schrödinger equation for the two isolated molecules,

\[ H_0 \Psi^{(o)} = E^{(o)} \Psi^{(o)} \]  \hspace{1cm} (1.1-3)

In Eq. (1.1-2) \( H \) and \( \Psi \) are, respectively, the Hamiltonian and wavefunction for the interacting molecular system and in Eq. (1.1-3) \( H_0 \) and \( \Psi^{(o)} \) are the Hamiltonian and wavefunction, respectively, for the isolated molecules.

Eq. (1.1-3) serves as the unperturbed or zeroth order problem in many perturbation theory treatments of intermolecular forces. This approach can satisfactorily treat
charge overlap effects\textsuperscript{4, 5} in intermolecular forces which are important in understanding\textsuperscript{5} the divergent nature of the usual $R^{-1}$ expansion\textsuperscript{1-3} of the interaction energy. However it is in general very difficult to incorporate electron exchange effects\textsuperscript{3, 6, 7} into the treatments\textsuperscript{8} and these effects become appreciable as the intermolecular separation decreases from large to small values of $R$.

If electron exchange effects between "a" and "b" are neglected, the Rayleigh-Schrödinger perturbation theory\textsuperscript{9}, see Sec. 2.1A, can be used to give an approximate solution to Eq. (1.1-2) providing one can solve the unperturbed problem of Eq. (1.1-3). Then the interaction energy can be expressed\textsuperscript{10} as a sum of perturbation energies in the form

$$E_{ab} = E^{(1)} + E^{(2)} + E^{(3)} + \cdots \cdots . \quad (1.1-4)$$

These energies are Coulomb energies\textsuperscript{5-7} since the electron exchange effects have been neglected. The $n$-th order perturbation energy, $E^{(n)}$, is $n$-th order in the perturbation, $V$, which is the Coulomb electrostatic interaction between the particles in "a" and the particles in "b" and is given by

$$V = H - H_0 . \quad (1.1-5)$$
Usually, in the study of the interaction energy for large internuclear separations charge overlap effects between the two interacting molecules are also neglected in addition to exchange effects. This leads to the multipole $R^{-1}$ expansion for the perturbation $^{11-13}$, see Sec. 2.2,

$$V = \sum_{m}^{\infty} V_m R^{-m} \tag{1.1-6}$$

and the $R^{-1}$ expansion for the interaction energy $^{1-3}$

$$E_{ab} = -\sum_{s}^{\infty} C_s R^{-s} \tag{1.1-7}$$

Energies obtained by using the multipole expansion for the perturbation, Eq. (1.1-6), are defined as the expanded interaction energies to distinguish $^{4,5}$ them from the non-expanded energies which are obtained by using the non-expanded $V$, Eq. (1.1-5), for the perturbation. The coefficients $V_m$ and $C_s$, in Eqs. (1.1-6) and (1.1-7) respectively, depend only on the properties of the isolated molecules. Thus the calculations of the interaction energy are simplified when charge overlap effects are neglected. However it is well known $^{14-17}$ that the $R^{-1}$ expansion of the interaction energy is an asymptotic divergent series with respect to the corresponding exact interaction energy. This asymptotic nature has been shown $^{4,5,18}$ to be a result
of the neglect of the charge overlap effects between the
two interacting molecules. In Sec. 2.3 some interactions
are considered, using the Unsöld's average energy approxi-
mation, as models for discussing how this asymptotic
behaviour depends on the nature of the interacting species.

In Sec. 2.4 the H(1s)-H\(^{+}\), He-He, H(1s)-H(1s) and
H(1s)-H(2s) interactions are considered as model systems
for investigating the use of the Padé approximation
method\(^{19,20}\) to remove some of the convergence difficulties
associated with the direct use of the R\(^{-1}\) expansion of the
interaction energy, Eq. (1.1-7). The computations are
based on the Unsöld's average energy approximation and on
exact results for the H(1s)-H\(^{+}\) interaction. The results
indicate that the Padé approximation method is a simple,
useful way to remove some of the difficulties associated
with the slow rate of convergence of the R\(^{-1}\) series but
that it does not alleviate the problems associated with the
asymptotic divergent nature of the series.

For smaller intermolecular separations, where the
electron exchange effects between "a" and "b" are not
negligible, one usually can not formulate a suitable zeroth
order problem, Eq. (1.1-3), for Rayleigh-Schrödinger
perturbation treatments of intermolecular forces. In
Sec. 3.1A the generalized Brillouin-Wigner perturbation
theory\textsuperscript{9,21,22}, which does not require the knowledge of a zeroth order problem, is reviewed through third order in the energy,

$$E = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} + \mathcal{E}^{(2)} + \mathcal{E}^{(3)} + \cdots . \quad (1.1-8)$$

Since calculations beyond first order in the energy in this theory are very difficult, the Unsöld's average energy approximation is used to simplify the general results, see Sec. 3.1B. These Unsöld's results are further simplified by introducing a modified Hamiltonian, $\tilde{H}$, in the second and third order energies, see Sec. 3.1C. This eliminates the difficulty of evaluating the matrix elements of $H^2$ and $H^3$ that occur in the usual Unsöld's results of Sec. 3.1B.

The modified generalized Brillouin-Wigner perturbation theory in the Unsöld's approximation, which is developed in Sec. 3.1, is used in Sec. 3.2 to calculate the interaction energy through second order for two interacting hydrogen atoms in various states,

$$\bar{E}_{ab} = \mathcal{E}^{(1)} + \mathcal{E}^{(2)} . \quad (1.1-9)$$

The results obtained are compared with available corresponding exact results to provide discussions on the usefulness of the modified perturbation technique.

It has been shown\textsuperscript{23,24} that the (fixed) one centre
calculations can give accurate results for the energies of homonuclear and heteronuclear diatomic molecules near their equilibrium separations although there are convergence problems\textsuperscript{23} with this approach. It has also been suggested by several authors that the rate of convergence depends\textsuperscript{25-27} on the value of the internuclear separation, \( R \), and the results tend\textsuperscript{27-29} to "misbehave" for large \( R \). In Sec. 4.1 these properties of the fixed one centre calculations are briefly reviewed and discussed.

In order to correct the misbehaviour for large \( R \) and to attempt to speed up the convergence of the (fixed) one centre calculations the fixed one centre method is modified, in Sec. 4.2, by allowing the expansion centre(s) to float freely along the internuclear axis as a function of \( R \). For diatomic molecules in which either "atom" \( a \) or \( b \) is a bare nucleus, there is only one floating centre. For diatomic molecules in which both \( a \) and \( b \) contain electrons, there must be two floating centres. The floating centre(s) method is discussed formally in Sec. 4.3 using a perturbation theory approach. A variational method approach to the floating centre(s) method is also outlined for use in test calculations discussed in Sec. 4.4.

In Sec. 4.4 the ground state \( H_2^+ \) and \( H_2 \) molecules are used as model systems for testing the feasibility of using
the floating centre(s) method to calculate the interaction energy for all $R$. The interaction energy, $\tilde{E}_{ab}$, is obtained from, see also Eq. (1.1-1),

$$E_{ab} = \tilde{E}_{ab} = \tilde{E} - E^{(o)}$$

(1.1-10)

where $\tilde{E}$ is the variational total energy for the system,

$$E_0 \leq \tilde{E} = \frac{\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle}$$

(1.1-11)

Here $E_0$ and $H$ are, respectively, the exact ground state energy and the Hamiltonian for the system under consideration. $\tilde{\Psi}$ is the trial wavefunction used in the variational floating centre(s) calculations for the system.

In this thesis, atomic units$^{30}$ are used throughout: the unit of energy is $e^2/a_0$ and the unit of length is $a_0$ where $e$ is protonic charge and $a_0$ the first Bohr radius of the hydrogen atom. The coordinate systems used are all right-handed coordinate systems$^2$, see Section 2.2.
2. MODEL STUDY OF CHARGE OVERLAP EFFECTS IN INTERMOLECULAR FORCES VIA PERTURBATION THEORY

In this chapter the perturbation theory approach to intermolecular forces neglecting exchange effects will be discussed in some detail. These perturbation techniques will be used to investigate the dependence of the second order charge overlap effects on the nature of interactions via Unsöld's approximation using He-He, H(ls)-H+, H(ls)-H(ls) and H(ls)-H(2s) as model systems. In Sec. 2.4 the possibility of using Padé approximant methods to sum the \( R^{-1} \) expansions of the interaction energy is investigated using the above systems as models.

2.1 A PERTURBATION THEORY APPROACH NEGLECTING ELECTRON EXCHANGE EFFECTS

In this section some perturbation theory methods are outlined which can be used to investigate charge overlap effects in intermolecular forces. These techniques are applied to some model problems discussed in subsequent sections of this work.
2.1A. **GENERAL RESULTS**

Consider a bimolecular system formed by the interaction of species "a", in state $u_a$, with species "b", in state $u'_b$. The species "a", which consists of a set of particles $\{p\}$ containing electrons $\{i\}$, and "b", which consists of a set of particles $\{q\}$ containing electrons $\{j\}$, can be molecules, atoms or ions and the separation between them is $R$. The non-relativistic Schrödinger equation for this system is

$$H \Psi = E \Psi \quad (2.1-1)$$

where $H$ is the non-relativistic Hamiltonian and $\Psi$ and $E$ the wavefunction and energy, respectively, for the system.

A perturbation theory solution for Eq. (2.1-1) can be developed in a straightforward way$^{10,31-33}$ if electron exchange effects$^6,7,10$ are neglected between "a" and "b". This implies that the particles associated with species "a" and "b" at $R = \infty$ remain associated with these species as $R$ becomes finite. Using this assumption it is easy to decompose the Hamiltonian, $H$, into physically meaningful parts;

$$H = H_0 + V \quad (2.1-2)$$

where
\[ H_0 = H_0^{(a)} + H_0^{(b)} \quad (2.1-3) \]

and

\[ V = \sum_{p,q} \frac{e_p e_q}{r_{pq}} \quad (2.1-4) \]

Here \( e_p \) and \( e_q \) are the charges of particles "p" and "q", respectively, and \( r_{pq} \) is the distance between these particles. \( V \) is therefore the Coulomb electrostatic interaction between the particles in "a" and the particles in "b" at the intermolecular distance \( R \). \( H_0 \) is the Hamiltonian for the system at infinite separation, \( R = \infty \). \( H_0^{(a)} \) is the electrostatic Hamiltonian for the isolated molecule "a" with eigenfunction \( \varphi_a(u) \) and energy \( \epsilon_a(v) \) for the state specified by the set of quantum numbers \( u_a \),

\[ H_0^{(a)} \varphi_a(u) = \epsilon_a(v) \varphi_a(u) \quad (2.1-5) \]

and similarly for molecule "b" in the state \( u_b \). The set of quantum numbers \( u = (v, \omega) \), where \( \omega \) specifies the degeneracy of the state.

The perturbation solution for Eq. (2.1-1) is obtained by expanding the energy and the wavefunction of the total system in orders of the perturbation \( V \) to yield

\[ E = \sum_{n=0}^{\infty} E^{(n)} \quad (2.1-6) \]
\[ \Psi = \sum_{n=0}^{\infty} \Psi^{(n)} \]  \hspace{2cm} (2.1-7)

where \( E^{(n)} \) and \( \Psi^{(n)} \) are, respectively, the \( n \)-th order energy and wavefunction for the interacting system. The zeroth order wavefunction and energy, \( n = 0 \), represent the system when the two molecules are not interacting (at \( R = \infty \)) and the explicit form of \( \Psi^{(0)} \) depends upon the nature of the interacting species (see below). The first order wavefunction satisfies the differential equation

\[ (H_0 - E^{(0)}) \Psi^{(1)} + (V - E^{(0)}) \Psi^{(0)} = 0 \]  \hspace{2cm} (2.1-8)

where

\[ E^{(1)} = \langle \Psi^{(0)} | V | \Psi^{(0)} \rangle \]  \hspace{2cm} (2.1-9)

If \( \Psi^{(1)} \) can be obtained explicitly, then the perturbed energy can be calculated through third order,

\[ E^{(2)} = \langle \Psi^{(0)} | V | \Psi^{(1)} \rangle \]  \hspace{2cm} (2.1-10)

\[ E^{(3)} = \langle \Psi^{(1)} | (V - E^{(0)}) | \Psi^{(0)} \rangle \]  \hspace{2cm} (2.1-11)

with the condition,

\[ \langle \Psi^{(1)} | \Psi^{(0)} \rangle = 0 \]  \hspace{2cm} (2.1-12)
The spectral expansion of the second order energy is required later in this thesis. This is easily obtained by expanding $\Psi^{(1)}$ in terms of the eigenfunction of $H_0$:

$$H_0 \Psi^{(1)} (K) = \varepsilon (K) \Psi^{(1)} (K)$$

$$\Psi^{(o)} = \sum_{K} C_k \Psi^{(1)} (K)$$

where

$$\Psi^{(1)} (K) = \varphi_a (u^o) \varphi_b (u^o)$$

$$\varepsilon (K) = \varepsilon_a (V^o) + \varepsilon_b (V^o)$$

In Eq. (2.1-14) the prime indicates that the zeroth order wavefunction(s) corresponding to $\varepsilon (K) = \varepsilon^{(o)}$ are omitted from the sum. Using Eq. (2.1-14) it is easy to show that

$$E^{(a)} = - \sum_{K} \left| \langle \Psi^{(o)} | V | \Psi^{(1)} (K) \rangle \right|^2 \frac{\varepsilon (K) - \varepsilon^{(o)}}{\varepsilon (K) - \varepsilon^{(o)}}$$

Expressions analogous to Eq. (2.1-8)-(2.1-11) and Eq. (2.1-17) are available for the higher order wavefunctions and energies. Once the perturbed energies are obtained the interaction energy through n-th order is given by

$$E_{ab} = E - E^{(o)} = E^{(1)} + E^{(2)} + E^{(3)} + \ldots + E^{(n)}$$
2.1B. NON-RESONANT (DIRECT) INTERACTIONS\textsuperscript{10,34-36}

If \( a \) and \( b \) are two like molecules in the same energy state, \( \nu = \nu' \) or \( a, b \) are unlike molecules in arbitrary states (in this case \( \nu \neq \nu' \)), the zeroth order wavefunction for the interaction can be written in the form

\[
\Psi^{(0)} = \varphi_a(u) \varphi_b(u') . \tag{2.1-19}
\]

Here summations over \( \omega_a, \omega_b \) are implied for the product \( \varphi_a(u) \varphi_b(u') \) if \( u \) and \( u' \) are degenerate states. In this work we explicitly consider only the interactions of atoms in non-degenerate states and so Eq. (2.1-19) can be used directly.

The zeroth and first order energies corresponding to Eq. (2.1-19) are given by

\[
E^{(0)} = \xi_a(\nu) + \xi_b(\nu') \tag{2.1-20}
\]

\[
E^{(1)} = \langle \varphi_a(u) \varphi_b(u') | V | \varphi_a(u) \varphi_b(u') \rangle . \tag{2.1-21}
\]

The second order energy can be written as\textsuperscript{5,10,31,37}

\[
E^{(2)} = E^{(2)}(\text{induction}) + E^{(2)}(\text{dispersion}) \tag{2.1-22}
\]

where

\[
E^{(2)}(\text{induction}) = E^{(2)}(a \rightarrow b) + E^{(2)}(b \rightarrow a) \tag{2.1-23}
\]
\[ E^{(a \rightarrow b)} = - \sum_{u' \neq u'} \frac{|\langle \phi_a(w) \phi_b(w') | V | \phi_a(w) \phi_b(u') \rangle|^2}{\epsilon_b(v') - \epsilon_b(v')} \]  \hspace{1cm} (2.1-24) \\

and

\[ E^{(\text{dispersion})} = - \sum \frac{|\langle \phi_a(w) \phi_b(w') | V | \phi_a(w') \phi_b(u') \rangle|^2}{\epsilon_a(v') + \epsilon_b(v') - E^{(o)}} \]  \hspace{1cm} (2.1-25) \\

The nonexpanded induction energy \( E^{(2)}(b \rightarrow a) \) is similar to \( E^{(2)}(a \rightarrow b) \) and is easily obtained.

2.1c. **Resonant Interactions** \(^{10, 34-36, 38}\)

If \( a, b \) are two like molecules in different energy states \( v \) and \( v' \), the zeroth order wavefunction for the interaction is written in the form

\[ \Psi_\beta^{(o)} = 2^{-1/2} \left( \phi_a(u) \phi_b(u') + \beta \phi_a(u') \phi_b(u) \right) \]  \hspace{1cm} (2.1-26) \\

Here the summations over \( w, w' \) are again implied if the interacting molecules are in degenerate energy states. \( \beta = \pm 1 \) depends on the parity of the states \( u \) and \( u' \), as well as on the number of electrons in the atoms and the spin of the molecular state \(^{39}\).
Using this wavefunction, the zeroth and first order energies can be written as \[10,36,38,39a;\]

\[E^{(0)} = \varepsilon_a(v) + \varepsilon_b(v') = \varepsilon_a(v') + \varepsilon_b(v)\]  

(2.1-27)

\[E^{(1)} = E^{(1)}_{\text{dir}} + \beta E^{(1)}_{\text{res}}\]  

(2.1-28)

where \(E^{(1)}_{\text{dir}}\) is the direct part of \(E^{(1)}\) and is given by Eq. (2.1-21). The resonance part of \(E^{(1)}\) is given by

\[E^{(1)}_{\text{res}} = \langle \varphi_u | V | \varphi_{u'} \rangle \]  

(2.1-29)

The second order energy can also be decomposed into direct and resonance contributions \(10,34-36,38\)

\[E^{(2)} = E^{(2)}_{\text{dir}} + \beta E^{(2)}_{\text{res}}\]  

(2.1-30)

where \(E^{(2)}_{\text{dir}}\) is given by Eqs. (2.1-22)-(2.1-25) and

\[E^{(2)}_{\text{res}} = \sum_{u''} \frac{\langle \varphi_{u''} | V | \varphi_{u''} \rangle \langle \varphi_{u''} | V | \varphi_{u''} \rangle - E^{(0)}}{\varepsilon_a(v'') + \varepsilon_b(v'') - E^{(0)}}\]  

(2.1-31)

where the prime over the summation sign indicates that states with \(u'' = u, u'' = u'\) or \(u'' = u', u'' = u\) simultaneously are omitted from sum. The second order resonance contribution, \(E^{(2)}_{\text{res}}\), can also be separated into induction and dispersion components [see for example Ref. (10) and Appendix A]. For the purpose of this work only the total
resonance contribution is required.

It must be pointed out that the energies discussed in this section, see Eq. (2.1-21)-(2.1-31), are the exact non-expanded \(^4,5\) interaction energies (see next section) since no approximations aside from neglecting electron exchange effects \(^5,10,31,33\) have been made. Charge overlap effects \(^4,5\) are included in these results since the multipole expansion (see also next section) of \(V\) has not been used. These exact non-expanded energies, \(E^{(n)}\), \(n > 0\), can be written in the form \(^4,40,41\)

\[
E^{(n)} = E^{(n)}_{R^{-1}} + E^{(n)}_{\exp(-R)} \tag{2.1-32}
\]

where \(E^{(n)}_{R^{-1}}\) is comprised of functions which possess asymptotic \(R^{-1}\) expansions for large \(R\) and \(R^{-N}, N > 0\). \(E^{(n)}_{\exp(-R)}\) is made up of functions having no asymptotic expansions and which vanish when exponentially decreasing terms of the argument \(R\) are ignored. It is \(E^{(n)}_{R^{-1}}\) that gives rise \(^4,40,41\) to the \(R^{-1}\) expansion for the \(n\)-th order energy when charge overlap effects are neglected; see Sec. 2.2, Eq. (2.2-7).

2.1D. **UNSOELD'S APPROXIMATION**

The second order energy, given by Eq. (2.1-17) and discussed in detail in Secs. 2.1B and 2.1C, is usually not easy to evaluate exactly due to the "summation" over all
the discrete and continuum states of the interacting molecules. However if one is only concerned about the relative trends in second order charge overlap effects from interaction to interaction, the Unsöld's average energy approximation\textsuperscript{42} can be used to simplify the calculation. Here one assumes the denominator in Eq. (2.1-17) is a constant, $\Delta$, and obtains\textsuperscript{1,10,17,32}, using the matrix sum rule,

$$\tilde{E}^{(2)} = \frac{-1}{\Delta} \left\{ \langle \Psi^{(0)} \mid V^3 \mid \Psi^{(0)} \rangle - (E^{(1)})^2 \right\} \tag{2.1-33}$$

where

$$E^{(1)} = \langle \Psi^{(0)} \mid V \mid \Psi^{(0)} \rangle \tag{2.1-34}$$

The tilde indicates that this equation is Unsöld's approximation for the exact total non-expanded second order energy. This approximate second order energy can also be separated into direct and resonant parts depending upon the nature of the interaction under consideration (see Sec. 2.3A).

For the interactions of interest in this work $E^{(1)}$ is an exponentially decreasing function of increasing $R$. The second order Unsöld's energy, Eq. (2.1-33), can be written in the form\textsuperscript{17,41,43-45}

$$\tilde{E}^{(2)} = \tilde{E}^{(2)}_{R^{-1}} + \tilde{E}^{(2)}_{\text{exp}(-R)} \tag{2.1-35}$$
where \( E_{R-1}^{(2)} \) and \( \tilde{E}_{\exp}^{(2)} \) are the Unsöld's equivalents of the \( E_{R-1}^{(2)} \) and \( E_{\exp}^{(2)} \) of Eq. (2.1-32) for \( n = 2 \).

The Unsöld's results for the higher order interaction energies, \( \tilde{E}^{(n)} \) for \( n > 2 \), are considerably more complicated than Eq. (2.1-33) and are not required for the purpose of this thesis; see however Chap. 3 and Ref. (17). It must also be pointed out here that there are many ways \(^{46,47}\) (see Chapter 3) to choose the Unsöld's average energy, \( \Delta \). However the actual choice of \( \Delta \) will not be of concern in this Chapter since only relative effects where \( \Delta \) cancels will be considered; see Sec. 2.3B.

### 2.2 THE MULTIPOLAR EXPANSION AND "LONG RANGE" INTERACTION ENERGIES

The usual perturbation treatment of long range intermolecular energies is based\(^{1,2,5,10,32,33}\) on an additional assumption, the neglect of charge overlap between "a" and "b". That is now we assume that the charge distributions of the interacting molecules do not overlap;

\[
R > (r_{ap} + r_{bq}) \tag{2.2-1}
\]

where \( r_{ap} \) is the distance from \( O_a \), the coordinate origin in charge distribution "a" (molecule a), to particle "p" and similarly for \( r_{bq} \); See Fig. (2.2-1). With this additional
Fig. (2.2-1) Coordinate axes used for the computation of molecular interaction energies. $O_a$ and $O_b$ are the origins for right handed coordinate systems, Cartesian $(X,Y,Z)$ or spherical polar $(r,\theta,\phi)$, in the two charge distributions "a" and "b" respectively.
assumption, the perturbation potential $V$ can be expanded in a multipole series\textsuperscript{10-13} in powers of $R^{-1}$;

$$V = \sum_{m=k_{ab}}^{\infty} V_m R^{-m} ; \quad k_{ab} \leq 3$$ (2.2-2)

$$V_m = \sum_{l_a=0}^{m-1} V(m, l_a)$$ (2.2-3)

$$V(m, l_a) = \sum_{\omega=-l_a}^{l_a} G(l_a, m, \omega) Q_\omega^{(a)} Q_\omega^{(b)}$$ (2.2-4)

$$G(l_a, m, \omega) = \frac{(-1)^l_b (m-1)! 4\pi}{[(2l_a+1)(2l_b+1)(l_a^2 - \omega)(l_a^2 + \omega)!(l_b^2 - \omega)!(l_b^2 + \omega)!]^{1/2}}$$ (2.2-5)

$$Q_\omega^{(a)} = \sum_{\rho} e_\rho \gamma_{\rho l_a}^\omega \gamma_{\rho}^{\omega} (\theta_\rho, \phi_\rho)$$ (2.2-6)

where $l_b = m - l_a - 1$ and $l_\omega$ is the lesser of $l_a$ and $l_b$. Here $Q_\omega^{(a)}$ is the $\omega$-th spherical component of the $2^{l_a}$-pole electrostatic multipole moment operator\textsuperscript{13,48,49} of molecule a. For example $l_a = 0$ corresponds to the charge of molecule a while $l_a = 1, 2, 3, 4$ correspond to the dipole, quadrupole, octapole and hexadecapole multipole moment operators respectively. The $Y_\lambda^\omega$ are the well known spherical
harmonic functions. The expansion coefficients of \( V \), the \( V_m \), are independent of \( R \) and are comprised of a sum of terms representing the interaction of the various "instantaneous" electrostatic multipoles of molecule \( a \) with those of molecule \( b \). The value of \( k_{ab} \) depends on the nature of the interaction. For the interaction of two ions \( k_{ab} = 1 \) and the lead term of the multipole expansion is the \( R^{-1} \) charge-charge \( (l_a = 0, l_b = 0) \) term. \( k_{ab} = 2 \) corresponds to an ion interacting with a neutral molecule and the lead term in the multipole expansion is the \( R^{-2} \) charge-dipole \( (l_a = 0, l_b = 1 \) or vice versa) term. \( k_{ab} = 3 \) occurs for the interaction of two neutral molecules and the lead term in the multipole expansion corresponds to the instantaneous \( R^{-3} \) dipole-dipole \( (l_a = 1, l_b = 1) \) interaction.

Substituting the expansion of \( V \), Eq. (2.2-2), into the perturbation expression for \( E^{(n)} \) one obtains \( 1,3,32 \) an \( R^{-1} \) expansion for the \( n \)-th order energy:

\[
\lim_{R \to \infty} E^{(n)}_{R^{-1}} = -\sum_{m=K}^{\infty} C_m^{(n)} R^{-m}, \quad n > 0 \tag{2.2-7}
\]

where \( K \) depends on the nature of interaction under consideration. The coefficients, \( C_m^{(n)} \), are independent of \( R \) and depend only on the properties of the isolated molecules \( 1,3,32 \). It should be emphasized that the multipole expansion of \( V \) and hence the \( R^{-1} \) expansions of \( E^{(n)} \) requires the
assumption of the neglect of charge overlap effects represented schematically by \( \lim R \to \infty \). Summing the \( E^{(n)} \) for \( n \geq 1 \), one obtains an \( R^{-1} \) expansion for the interaction energy:

\[
E_{ab} = - \sum_{S=K_{ab}}^{\infty} C_{S} R^{-S}
\]  

(2.2-8)

where \( K_{ab} \) also depends on the nature of the interaction. For example, for the interaction of two neutral non-degenerate atoms, \( K_{ab} = 6 \) and the lead term in Eq. (2.2-8) is the London dipole-dipole dispersion energy\(^{52,53}\). For an ion interacting with a non-degenerate atom, \( K_{ab} = 4 \) and the lead term is the charge-induced dipole interaction energy\(^{1,2}\). The individual \( C_{S} \), which are sums of the \( C_{m}^{(n)} \), depend only on the properties of the isolated molecules.

If one substitutes the multipole expansion of \( V \) into Eq. (2.1-33), one obtains an \( R^{-1} \) expansion for the Unsöld's second order energy; see also Eq. (2.1-35),

\[
\lim_{R \to \infty} E^{(2)}_{R \to \infty} = \lim_{R \to \infty} E^{(2)}_{R^{-1}} = - \sum_{m=K}^{\infty} C_{m}^{(2)} R^{-m}
\]  

(2.2-9)

These Unsöld's \( R^{-1} \) results are very useful in discussing trends in second order charge overlap effects, see Sec. 2.3, since the coefficients \( \tilde{C}_{m}^{(2)} \) are much easier to obtain than the exact second order expansion coefficients \( C_{m}^{(2)} \).
The growth of the coefficients, $\tilde{c}_m^{(2)}$ and $c_m^{(n)}$, is usually very fast as a function of $m$, see Sec. 2.3B and Ref. (41). Indeed the series representations of $\tilde{E}^{(2)}$, Eq. (2.2-9), and $E^{(n)}$, Eq. (2.2-7), are divergent asymptotic series. If these series representations of the interaction energies are to be meaningful\textsuperscript{5,18,54} the higher order terms in the $R^{-1}$ expansions must be considerably smaller than the lower order terms. These properties will be discussed in detail in Sec. 2.3B, see also Ref. (55).

2.3 SECOND ORDER CHARGE OVERLAP EFFECTS IN UNSÖLD'S APPROXIMATION

The long-range $R^{-1}$ expansions of the interaction energy are very convenient to use and easier to calculate\textsuperscript{2,3,32} than the corresponding results including charge overlap or exchange effects. However as pointed out by Coulson and Gillam\textsuperscript{14}, Brooks\textsuperscript{16}, Roe\textsuperscript{15}, and Dalgarno and Lewis\textsuperscript{17} the long range $R^{-1}$ expression is asymptotically divergent for all finite values of $R$; see also Refs. (4,10,32). As discussed by Kreek and Meath\textsuperscript{5} and Singh, Kreek and Meath\textsuperscript{18} this divergence is caused by the neglect of charge overlap effects in the usual long range treatments. Clearly the effects of this assumption must depend markedly upon the nature of the interacting species. A complete discussion
of second order charge overlap effects for the ground state He-He, H(1s)-H$^+$ and H(1s)-H(1s) interactions has been given by Kreek$^{47}$, see also Ref. (55). In this section the H(1s)-H(2s) interaction is considered, using Unsöld's approximation, as a model system for studying second order charge overlap effects for excited state interactions. These results are compared with the results of Kreek, mentioned above, to give a more comprehensive discussion of the dependence of charge overlap effects on the nature of interaction.

2.3A THE NON-EXPANDED AND EXPANDED SECOND ORDER ENERGIES IN UNSÖLD'S APPROXIMATION FOR THE H(1s)-H(2s) INTERACTION

For the H(1s)-H(2s) interaction the zeroth order wavefunctions, neglecting electron exchange, are taken to be, see Eq. (2.1-26),

$$
\Psi_+^{(0)} = 2^{1/2} \left[ \hat{a}(1) \hat{b}(2) \pm \hat{a}(1) \hat{b}(2) \right]
$$

(2.3-1)

where $a(1)$ and $\hat{a}(1)$ are normalized "1s" and "2s" hydrogen atom wavefunctions, respectively, centred on proton "a". The upper and lower signs in $\Psi^{(0)}$ correspond to the $^1\Sigma_g^+$ ($^3\Sigma_u^+$) and $^1\Sigma_u^+$ ($^3\Sigma_g^+$) states$^{36,38,39,56}$, respectively,
of the molecule formed by the interaction.† The mixing between \(1s2s\) and \(1s2p_{\sigma}\) configurations has been neglected in the wavefunctions, \(\psi^{(0)}_{\pm}\), since it is not important until \(R \lesssim 12\ a_0\) (see Appendix B) and vanishes when the multipole expansion of \(V\) is used\(^{39,55,56}\). The configuration mixing, therefore, will not affect the trends in the charge overlap effects appreciably until \(R \lesssim 12\ a_0\).

The interaction potential energy for this interaction is

\[
V = -\frac{1}{\gamma_{a2}} - \frac{1}{\gamma_{b1}} + \frac{1}{\gamma_{12}} + \frac{1}{R}
\]

(2.3-2)

where 1 and 2 represent electrons associated with protons "a" and "b" respectively. Substituting the wavefunction, Eq. (2.3-1), into Eq. (2.1-33) one obtains the Unsöld's non-expanded second order energy given by

\[
\tilde{E}^{(2)} = \tilde{E}_{R^{-1}}^{(2)} + \tilde{E}_{\text{exp}(-R)}^{(2)}
\]

(2.3-3a)

† The wavefunctions, \(\psi^{(0)}_{\pm}\), do not necessarily have "gerade" or "ungerade" symmetry\(^{39}\). \(\psi_{\pm}\) and \(\psi_{\mp}\) correspond to the \(1\Sigma_g^+(3\Sigma_u^+\) and \(1\Sigma_u^+(3\Sigma_g^+)\) symmetries respectively when they are properly antisymmetrized with respect to the exchange of electrons between "a" and "b". When electron exchange and relativistic effects are neglected the singlet states are degenerate with the triplet states in the corresponding bracket.
\[ \tilde{E}^{(2)} = E^{(2)}_{\text{dir}} + E^{(2)}_{\text{res}} \]  \hspace{1cm} (2.3-3b)

\[ \tilde{E}^{(2)}_{\text{dir}} = \frac{1}{\Delta} \left\{ \langle a^{(1)} b^{(2)} | V^2 | a^{(1)} b^{(2)} \rangle - (E^{(0)}_{\text{dir}})^2 \right\} \]  \hspace{1cm} (2.3-4)

\[ \tilde{E}^{(2)}_{\text{res}} = \frac{1}{\Delta} \left\{ \langle a^{(1)} b^{(2)} | V^2 | a^{(1)} b^{(2)} \rangle + (E^{(0)}_{\text{res}})^2 - 2E^{(1)}_{\text{dir}} E^{(0)}_{\text{res}} \right\} \]  \hspace{1cm} (2.3-5)

where the first order direct and resonant energies for the interaction are given by

\[ E^{(1)}_{\text{dir}} = \langle a^{(1)} b^{(2)} | V | a^{(1)} b^{(2)} \rangle \]  \hspace{1cm} (2.3-6)

\[ E^{(1)}_{\text{res}} = \langle a^{(1)} b^{(2)} | V | a^{(1)} b^{(2)} \rangle \]  \hspace{1cm} (2.3-7)

Here the average energy \( \Delta \) can be different for \( \tilde{E}^{(2)}_{\text{dir}} \) and \( \tilde{E}^{(2)}_{\text{res}} \) since these results can be obtained directly by applying Unsöld's approximation separately to the exact direct second order energy, Eq. (2.1-22), and the exact resonant second order energy, Eq. (2.1-31). The evaluation of the integrals occurring in Eqs. (2.3-4)-(2.3-7) is discussed in Appendix C and analytical results for \( \tilde{E}^{(2)} \).
\( \tilde{E}^{(2)}_{R^{-1}}, \tilde{E}^{(2)}_{\exp(-R)}, \tilde{E}^{(2)}_{\text{dir}}, \) and \( \tilde{E}^{(2)}_{\text{res}} \) are also given there. Numerical results for these energies are shown in Table (2.3-1) as a function of \( R \). One can see the relative importance of each contribution in \( \tilde{E}^{(2)}_{\text{res}} \) from the table; for example \( \tilde{E}^{(2)}_{\text{res}} \) is about 1 percent of \( \tilde{E}^{(2)}_{\text{dir}} \) at \( R = 2a_0 \), 3 per cent at \( R = 10a_0 \), and 6 per cent at \( R = 20a_0 \). The importance of \( \tilde{E}^{(2)}_{R^{-1}} \) and \( \tilde{E}^{(2)}_{\exp(-R)} \) will be discussed in detail in Sec. 2.3C.

The long range \( R^{-1} \) expansion of \( \tilde{E}^{(2)} \) can be obtained by using the multipole expansion, Eq. (2.2-2), for \( V \) in Eqs. (2.3-3)-(2.3-5). In this case charge overlap effects as well as the electron exchange effects are neglected, \( E^{(1)} \) vanishes, and one obtains

\[
\lim_{R \to \infty} \tilde{E}^{(2)} = \lim_{R \to \infty} \tilde{E}^{(2)}_{R^{-1}} = - \sum_{m=3}^{\infty} \tilde{C}^{(2)}_{2m} R^{-2m} = - \sum_{m=3}^{\infty} \tilde{U}_{2m} \tag{2.3-8}
\]

The Unsöld's expansion coefficients, \( \tilde{C}^{(2)}_{2m} \), in Eq. (2.3-8) are approximations to the exact coefficients \( C^{(2)}_{2m} \) and for this interaction only even powers of \( R^{-1} \) occur in the multipole result for \( \tilde{E}^{(2)} \). The evaluation of the \( \tilde{C}^{(2)}_{2m} \), which also has direct and resonant parts, is discussed in Appendix D and the results are

\[
\tilde{C}^{(2)}_{2m} = \tilde{C}^{(2)}_{2m}(\text{direct}) \pm \tilde{C}^{(2)}_{2m}(\text{resonance}) \tag{2.3-9}
\]
Table (2.3-1) Second Order Energies in Units of the Unsöld's Average Energy $\Delta$ for the H(1s)–H(2s) Interaction as a Function of R. The figures in parentheses indicate powers of ten.

<table>
<thead>
<tr>
<th>R</th>
<th>$\tilde{E}^{(2)}_{\text{dir}}$</th>
<th>$\tilde{E}^{(2)}_{\text{res}}$</th>
<th>$\tilde{E}^{(2)}<em>{\text{dir}} + \tilde{E}^{(2)}</em>{\text{res}}$</th>
<th>$\tilde{E}^{(2)}<em>{\text{dir}} + \tilde{E}^{(2)}</em>{\text{res}}/R^{-1}$</th>
<th>$\tilde{E}^{(2)}<em>{\text{dir}} - \tilde{E}^{(2)}</em>{\text{res}}$</th>
<th>$\tilde{E}^{(2)}<em>{\text{dir}} - \tilde{E}^{(2)}</em>{\text{res}}/R^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.7485 (-1)</td>
<td>0.9099 (-3)</td>
<td>0.7576 (-1)</td>
<td>-0.3465 (-1)</td>
<td>0.7388 (-1)</td>
<td>-0.4717 (-1)</td>
</tr>
<tr>
<td>4</td>
<td>0.1454 (-1)</td>
<td>0.8391 (-3)</td>
<td>0.1538 (-1)</td>
<td>-0.9605 (-2)</td>
<td>0.1370 (-1)</td>
<td>-0.6658 (-2)</td>
</tr>
<tr>
<td>6</td>
<td>0.6403 (-2)</td>
<td>0.2926 (-3)</td>
<td>0.6695 (-2)</td>
<td>-0.2239 (-2)</td>
<td>0.6110 (-2)</td>
<td>-0.1794 (-2)</td>
</tr>
<tr>
<td>8</td>
<td>0.2245 (-2)</td>
<td>0.8161 (-4)</td>
<td>0.2326 (-2)</td>
<td>-0.2057 (-3)</td>
<td>0.2163 (-2)</td>
<td>-0.2394 (-3)</td>
</tr>
<tr>
<td>10</td>
<td>0.6550 (-3)</td>
<td>0.1980 (-4)</td>
<td>0.6748 (-3)</td>
<td>0.7472 (-4)</td>
<td>0.6352 (-3)</td>
<td>0.4797 (-4)</td>
</tr>
<tr>
<td>12</td>
<td>0.1760 (-3)</td>
<td>0.4930 (-5)</td>
<td>0.1809 (-3)</td>
<td>0.5406 (-4)</td>
<td>0.1710 (-3)</td>
<td>0.4531 (-4)</td>
</tr>
<tr>
<td>14</td>
<td>0.4754 (-4)</td>
<td>0.1461 (-5)</td>
<td>0.4900 (-4)</td>
<td>0.2419 (-4)</td>
<td>0.4608 (-4)</td>
<td>0.2136 (-4)</td>
</tr>
<tr>
<td>16</td>
<td>0.1412 (-4)</td>
<td>0.5380 (-6)</td>
<td>0.1465 (-4)</td>
<td>0.1006 (-4)</td>
<td>0.1358 (-4)</td>
<td>0.8993 (-5)</td>
</tr>
<tr>
<td>18</td>
<td>0.4953 (-5)</td>
<td>0.2360 (-6)</td>
<td>0.5189 (-5)</td>
<td>0.4373 (-5)</td>
<td>0.4717 (-5)</td>
<td>0.3902 (-5)</td>
</tr>
<tr>
<td>20</td>
<td>0.2094 (-5)</td>
<td>0.1168 (-6)</td>
<td>0.2211 (-5)</td>
<td>0.2071 (-5)</td>
<td>0.1977 (-5)</td>
<td>0.1837 (-5)</td>
</tr>
<tr>
<td>22</td>
<td>0.1032 (-5)</td>
<td>0.6289 (-7)</td>
<td>0.1095 (-5)</td>
<td>0.1071 (-5)</td>
<td>0.1071 (-5)</td>
<td>0.1837 (-5)</td>
</tr>
<tr>
<td>24</td>
<td>0.5653 (-6)</td>
<td>0.3609 (-7)</td>
<td>0.6104 (-6)</td>
<td>0.5975 (-6)</td>
<td>0.5292 (-6)</td>
<td>0.5254 (-6)</td>
</tr>
<tr>
<td>26</td>
<td>0.3327 (-6)</td>
<td>0.2178 (-7)</td>
<td>0.3545 (-6)</td>
<td>0.3538 (-6)</td>
<td>0.3109 (-6)</td>
<td>0.3103 (-6)</td>
</tr>
<tr>
<td>28</td>
<td>0.2061 (-6)</td>
<td>0.1370 (-7)</td>
<td>0.2198 (-6)</td>
<td>0.2197 (-6)</td>
<td>0.1924 (-6)</td>
<td>0.1923 (-6)</td>
</tr>
<tr>
<td>30</td>
<td>0.1329 (-6)</td>
<td>0.8921 (-8)</td>
<td>0.1418 (-6)</td>
<td>0.1418 (-6)</td>
<td>0.1239 (-6)</td>
<td>0.1239 (-6)</td>
</tr>
</tbody>
</table>
where

\[ C_{2m}^{(2)}(\text{direct}) = \frac{(2m-2)!}{162 \Delta} \left[ 126 m^3 - 639 m^2 + 1407 m - 1312 + (41 - 9m) 2^{5-2m} \right] \tag{2.3-10} \]

\[ C_{2m}^{(2)}(\text{resonance}) = \frac{2m(2m-2)!}{5 \Delta} (m^4 - 5 m^2 + 4) \left( \frac{2}{3} \right)^{2m+7} \tag{2.3-11} \]

In Table (2.3-2) the ratio, \([C_{2m}^{(2)}(\text{resonance})/C_{2m}^{(2)}(\text{direct})]\), is given as a function of \(m\). The corresponding ratios for the available exact results \(^{36,56}\) are given in parentheses for comparison. It can be seen from the table that the resonant contribution becomes less important with respect to the direct contribution as \(m\) increases and finally becomes negligible with respect to the direct part although the resonant part itself is still a large quantity.

2.3B \hspace{1em} \text{DEPENDENCE OF SECOND ORDER CHARGE OVERLAP EFFECTS ON THE NATURE OF INTERACTION USING MODEL INTERACTIONS AS EXAMPLES}

The Unsöld's non-expanded and expanded second order energies for the \(H(1s)-H^+, \text{He-He}, H(1s)-H(1s)\) and \(H(1s)-H(2s)\) interactions can all be written in the form \(^{55}\).
Table (2.3-2) Comparison of the resonant Unsöld's expansion coefficient, Eq. (2.3-11), with the direct Unsöld's expansion coefficient, Eq. (2.3-10), as a function of \( m \). The corresponding exact results\(^{36} \) are given in square brackets for comparison.

<table>
<thead>
<tr>
<th>( m )</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>15</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tilde{C}_{2m}^{(2)} ) (res.)</td>
<td>0.70 (-1)</td>
<td>0.49 (-1)</td>
<td>0.30 (-1)</td>
<td>0.17 (-1)</td>
<td>0.52 (-2)</td>
<td>0.14 (-2)</td>
<td>0.49 (-4)</td>
<td>0</td>
</tr>
<tr>
<td>( \tilde{C}_{2m}^{(2)} ) (dir.)</td>
<td>[0.16 (0)]</td>
<td>[0.82 (-1)]</td>
<td>[0.68 (-1)]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ \tilde{E}^{(2)} = \tilde{E}_{R^{-1}}^{(2)} + \tilde{E}_{\exp(-R)}^{(2)} \quad (2.3-12) \]

and

\[ \lim_{R \to \infty} \tilde{E}_{R^{-1}}^{(2)} = - \sum_{m=K}^{\infty} \tilde{C}_{2m}^{(2)} R^{-2m} = - \sum_{m=K}^{\infty} \tilde{U}_{2m} \quad (2.3-13) \]

Here \( K = 2 \) for the \( \text{H}(1s) - \text{H}^+ \) interaction, \( K = 3 \) for all the other interactions. It must also be pointed out here that the coefficients, \( \tilde{C}_{2m}^{(2)} \), contain \( \Delta \) and only even powers of \( R^{-1} \) occur in the multipole results of \( \tilde{E}^{(2)} \) for the interactions considered here. The results for \( \tilde{E}^{(2)} \), \( \tilde{E}_{R^{-1}}^{(2)} \), \( \tilde{E}_{\exp(-R)}^{(2)} \), and \( \tilde{C}_{2m}^{(2)} \), for all \( m \), for the \( \text{H}(1s) - \text{H}^+ \), \( \text{He-He} \), \( \text{H}(1s) - \text{H}(1s) \) interactions, can be obtained from Refs. (17, 43, 44), see also Ref. (55). The corresponding results for the \( \text{H}(1s) - \text{H}(2s) \) interaction are given in Sec. 2.3A and Appendices C and D. In this section these four interactions are used as models to discuss the dependence of charge overlap effects on the nature of interaction. This discussion supplements that of Kreek\(^{47}\) who considered the \( \text{H}(1s) - \text{H}^+ \), \( \text{He-He} \), \( \text{He-}\text{H}(1s) \) and \( \text{H}(1s) - \text{H}(1s) \) interactions in considerable detail.
In Table (2.3-3) the ratios of the coefficients of successive terms in $R^{-1}$ expansion of the Unsöld's approximation for the second order energy, $\left[ \frac{\tilde{C}_{2m+2}^{(2)}}{\tilde{C}_{2m}^{(2)}} \right]$, are given for the various interactions as a function of $m$. The available ratios corresponding to the exact coefficient\textsuperscript{36, 40,56-58}, $C_{2m}^{(2)}$, are given in parenthesis. The agreement between the Unsöld's and the exact ratios is quite good. This indicates that the series, Eq. (2.2-9), can be expected to demonstrate the asymptotic properties of the exact series, Eq. (2.2-8), in a reasonable way.

Severe convergence problems arise in the $R^{-1}$ expansion of the interaction energy. Using the ratio test and the limiting value of $\left[ \frac{\tilde{C}_{2m+2}^{(2)}}{\tilde{C}_{2m}^{(2)}} \right]$ as $m \to \infty$, see Table (2.3-3), it can be shown that the $R^{-1}$ expansion of $\tilde{E}^{(2)}$, for all the interactions considered here, are divergent for all finite values of $R$. This property is also undoubtedly true for the exact expansions as well (see for example Sec. 2.4) but the $C_{2m}^{(2)}$ are available for all $m$ only for a few very simple one electron interactions\textsuperscript{40}.

The values of $R$ for which successive terms in the $R^{-1}$ expansion become equal are given by the square root of the entries in Table (2.3-3):

$$\tilde{U}_{2m+2} = \tilde{U}_{2m} \quad (2.3-14)$$

when
Table (2.3-3) Ratios of the Coefficients of Successive Terms in the $R^{-1}$ Expansion of Some Second-Order Dispersion Energies

<table>
<thead>
<tr>
<th>$\frac{C^{(2)}<em>{2m+2}}{C^{(2)}</em>{2m}}$</th>
<th>m=3</th>
<th>m=4</th>
<th>m=6</th>
<th>m=8</th>
<th>m=10</th>
<th>m=12</th>
<th>m$^{-\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-He $^{a,b}$</td>
<td>7.9</td>
<td>10.2</td>
<td>18.4</td>
<td>29.8</td>
<td>44.0</td>
<td>61.1</td>
<td>$m^2/(\frac{27}{16})^2$</td>
</tr>
<tr>
<td>(9.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(1s)-H$^{+}$$^{c}$</td>
<td>10</td>
<td>17.5</td>
<td>38.5</td>
<td>67.5</td>
<td>104.5</td>
<td>149.5</td>
<td>$m^2$</td>
</tr>
<tr>
<td>(11.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(1s)-H(1s)$^{a}$</td>
<td>22.5</td>
<td>29.2</td>
<td>52.5</td>
<td>84.8</td>
<td>125.4</td>
<td>174.1</td>
<td>$m^2$</td>
</tr>
<tr>
<td>(19.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(1s)-H(2s) $^{1}\Sigma_g^+$</td>
<td>111.9</td>
<td>140.1</td>
<td>236.1</td>
<td>367.0</td>
<td>530.4</td>
<td>725.8</td>
<td>$m^2$</td>
</tr>
<tr>
<td>(95.7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(1s)-H(2s) $^{1}\Sigma_u^+$</td>
<td>116.7</td>
<td>145.7</td>
<td>239.8</td>
<td>368.8</td>
<td>531.1</td>
<td>726.1</td>
<td>$m^2$</td>
</tr>
<tr>
<td>(111.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Results from Kreek, Ref. (47)
b. Screening constant, s = 27/16
c. From Ref. (17)
\[ R = R_m = \left( \frac{C_{2m+2}^{(2)}}{C_{2m}^{(2)}} \right)^{1/2} \]  

(2.3-15)

The values of \( R_m \) increase markedly for the higher-order multipole interactions, that is \( R_m \) increases rapidly as a function of \( m \), see Table (2.3-3). More important however is the pronounced increase in the divergence of the multipole results as one proceeds down the table from the He-He interaction to the H(1s)-H(2s) interaction; for any fixed value of \( m \), \( R_m \) increases rapidly from the top to the bottom of Table (2.3-3). For example, for the He-He interaction \( R_3 = 2.8, R_4 = 3.2, R_6 = 4.3 \) while for the \( 1\Sigma^+ \) H(1s)-H(2s) interaction \( R_3 = 10.6, R_4 = 11.8, R_6 = 15.4 \). These trends are in agreement with the fact that neglect of charge overlap effects is responsible \(^5,18\) for the divergence problem in the \( R^{-1} \) expansions and that charge overlap between the interacting species, for a given value of \( R \), is more pronounced for interactions involving "large" or "excited" systems.

Strictly speaking the \( R^{-1} \) expansion is asymptotic to \( \tilde{E}_{R^{-1}}^{(2)} \) and not to the total non-expanded second order energy \( \tilde{E}^{(2)} \); see Eqs. (2.3-3a) and (2.3-8). The function \( \tilde{E}_{R^{-1}}^{(2)} \) is comprised of functions of the form \( R^{-N}, N > 0, \exp(-cR)Ei(cR) \).
and \( \exp(cR) \text{Ei}(-cR) \), \( c > 0 \), \(^\dagger\) which possess asymptotic expansions for large \( R \), while \( \tilde{E}^{(2)}_{\exp(-R)} \) is made up of functions which have no asymptotic expansions, see Sec. 2.1. Hence the \( R^{-1} \) expansion is rigorously an asymptotic approximation to \( \tilde{E}^{(2)} \) only when \( \tilde{E}^{(2)}_{\exp(-R)} \) is considerably smaller in magnitude than \( \tilde{E}^{(2)}_{R^{-1}} \). The importance of the \( \tilde{E}^{(2)}_{\exp(-R)} \) can be seen graphically for all the interactions in Fig. (2.3-1) where the ratios, \( \tilde{E}^{(2)}_{R^{-1}}/\tilde{E}^{(2)} \), are plotted as a function of \( R \). Numerical results of \( \tilde{E}^{(2)}_{R^{-1}} \) and \( \tilde{E}^{(2)}_{\exp(-R)} \) can be obtained as a function of \( R \) from the data in Table (2.3-1) for the H(1s)-H(2s) interaction.

Define the partial sum

\[
\tilde{S}(\omega) = - \sum_{m=K}^{\omega+K} \tilde{C}_{2m} R^{-2m}
\]  

(2.3-16)

which is a truncated \( R^{-1} \) expansion of \( \tilde{E}^{(2)} \), Eq. (2.3-13).

Ratios of the form

\[
\tilde{E}(\omega) = \tilde{S}(\omega)/\tilde{E}^{(2)}
\]  

(2.3-17)

and

\(^\dagger\) The \( \text{Ei}(x) \) and \( \text{Ei}(-x) \), \( x = cR \), are exponential integrals defined by \(^{59}\) \( \text{Ei}(x) = - \int_{-\infty}^{\omega} t^{-1} \exp(-t)dt \) and

\[
\text{Ei}(-x) = - \int_{x}^{\infty} t^{-1} \exp(-t)dt = - E_1(x).
\]
Fig. (2.3-1) A comparison of the ratio, $\frac{E^{(2)}_{R-1}}{E^{(2)}}$, as a function of $R$ for the various interactions considered in Sec. 2.3.
\[ \tilde{E}(\omega) = \frac{S(\omega)}{E_{R^{-1}}^{(2)}} \] (2.3-18)

are compared as a function of R and \( \omega \) in Figs. (2.3-2)-(2.3-5) for the \( \text{H}(1s)^{+}-\text{H}, \text{He}-\text{He}, \text{H}(1s)-\text{H}(1s) \) and \( \text{H}(1s)-\text{H}(2s) \) interactions respectively. Comparing these figures it is easy to see that for values of R where the \( R^{-1} \) expansions have meaning\(^5,18,54\) (see below), the partial sums, \( \tilde{S}(\omega) \), represent \( \tilde{E}_{R^{-1}}^{(2)} \) much more accurately than \( \tilde{E}^{(2)} \) itself until R is sufficiently large that \( \tilde{E}_{\exp(-R)}^{(2)} \) is negligible with respect to \( \tilde{E}_{R^{-1}}^{(2)} \).

The asymptotic nature of the \( R^{-1} \) expansion of the second order energy, \( \tilde{E}^{(2)} \), can be seen clearly from Figs. (2.3-2)-(2.3-5). The asymptotic behaviour of these expansions is similar for all these interactions. However the values of R where the divergent nature of the series becomes readily apparent depends on the nature of the interacting species; see also the values of \( R_m \) discussed above. If the series representation of the interaction energy is to be meaningful the higher order terms in the \( R^{-1} \) expansion must be considerably smaller than the lower order terms\(^5\); see also for example Refs. (18,54,55). From Figs. (2.3-2)-(2.3-5), this is clearly not the case for all \( \omega \) and R. This condition places a practical upper limit on
Fig. (2.3-2) A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s)-\text{H}^+$ interaction in Unsöld's approximation. (a) $\tilde{S}(\omega)/\tilde{E}_{R-1}^{(2)}$ (b) $\tilde{S}(\omega)/\tilde{E}^{(2)}$. The value of $\omega$ is indicated on the graph.
Fig. (2.3-3) A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the He-He interaction in Unsöld's approximation. (a) $\tilde{S}(\omega)/\tilde{E}^{(2)}_{R-1}$ (b) $\tilde{S}(\omega)/\tilde{E}^{(2)}$. The value of $\omega$ is indicated on the graph.
Fig. (2.3-4) A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)–H(1s) interaction in Unsöld's approximation. (a) $\tilde{S}(w)/\tilde{E}_{R-1}^{(2)}$ (b) $\tilde{S}(w)/\tilde{E}^{(2)}$. The value of w is indicated on the graph.
Fig. (2.3-5) A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $H(1s)-H(2s)$ interaction in Unsöld's approximation. (a) $\tilde{S}(\omega)/\tilde{E}_R^{(2)}$ (b) $\tilde{S}(\omega)/\tilde{E}_R^{(2)}$. The value of $\omega$ is indicated on the graph.
\( \omega \) in Eq. (2.3-16) as a function of \( R \) as is easily seen from Figs. (2.3-2)-(2.3-5). For a given value of \( \omega \) the expansion agrees well with the exact results for \( \tilde{E}^{(2)}_{R^{-1}} \) (and \( \tilde{E}^{(2)} \)) for large enough \( R \), but as \( R \) becomes smaller the series tends to overestimate the exact results and diverges rapidly as \( R \) decreases. The asymptotic nature of the \( R^{-1} \) multipole series is clear; that is for values of \( R \) outside the region of validity of the expansion including more terms in the series yields a poorer approximation to the exact results.

It should be pointed out\(^{55}\) that for intermediate values of \( R \), the convergence of the series to the exact results is quite slow as a function of \( \omega \). For example, \( \tilde{S}(1), \tilde{S}(2) \) and \( \tilde{S}(3) \) are in error with respect to \( \tilde{E}^{(2)} \) by 40, 20 and 10 per cent respectively at \( R \sim 20a_0 \) for the \( H(1s)-H(2s) \) interaction and are in error by 25, 10 and 5 per cent respectively for the \( \text{He-He} \) interaction at \( R \sim 6a_0 \). This illustrates a more practical problem that can arise in using the \( R^{-1} \) series to represent \( E^{(2)} \) since usually only the first few terms in the series are known accurately for most interactions. Thus the usefulness of \( R^{-1} \) expansions is limited in two ways. The asymptotic nature of the expansion and the importance of \( \tilde{E}^{(2)}_{\exp(-R)} \) limits its usefulness for "small" values of \( R \), while the slow rate of
convergence of the series limits its usefulness for "intermediate" values of $R$. Some techniques for improving the convergence for the important intermediate values of $R$ are discussed in Sec. 2.4.

2.3C  SECOND ORDER CHARGE OVERLAP EFFECTS USING THE EXACT TREATMENT OF THE H(1s)-H$^+$ INTERACTION

The exact results for the non-expanded and expanded second order energy $E^{(2)}$, can be written in the form, see also Secs. 2.1 and 2.2:

$$E^{(2)} = E^{(2)}_{R^{-1}} + E^{(2)}_{\exp(-R)} \tag{2.3-19}$$

and

$$\lim_{R \to \infty} E^{(2)}_{R^{-1}} = \lim_{R \to \infty} E^{(2)}_{\exp(-R)} = -\sum_{m=K}^{\infty} C^{(2)}_{2m} R^{-2m} \tag{2.3-20}$$

Here we consider the H(1s)-H$^+$ interaction$^{40}$ where $K = 2$ and only the even powers of $R^{-1}$ occur in Eq. (2.3-20).

Results for $E^{(2)}_{R^{-1}}$, $E^{(2)}_{\exp(-R)}$ and $C^{(2)}_{2m}$ for this interaction can be obtained from Coulson$^{14}$, Dalgarno and Lynn$^{40}$ and Robinson$^{60}$. The series, Eq. (2.3-20), like its Unsöld's equivalent, is divergent for all finite values of $R$. This can be shown by the ratio test using the limiting value of $[\tilde{C}^{(2)}_{2m+2}/\tilde{C}^{(2)}_{2m}]$ as $m \to \infty$;
Define the partial sum

$$S(\omega) = -\sum_{m=2}^{\omega+2} C_{2m}^{(2)} R^{-2m}$$

(2.3-22)

a truncated $R^{-1}$ expansion of the exact $E^{(2)}$ for the

$H(1s)$-$H^+$ interaction. Ratios of the form

$$E(\omega) = S(\omega)/E^{(2)}$$

(2.3-23)

and

$$E_{R^{-1}}(\omega) = S(\omega)/E^{(2)}_{R^{-1}}$$

(2.3-24)

are shown as a function of $R$ and $\omega$ in Fig. (2.3-6). The
trends for the representation of $E^{(2)}_{R^{-1}}$ are very similar to
those for the Unsöld's calculation for the $H(1s)$-$H^+$ inter-
action; compare Fig. (2.3-6a) and (2.3-2a). However, the
graphs corresponding to the representation of the total
second order energy are markedly different, see Fig. (2.3-6b)
and (2.3-2b), since $\bar{E}^{(2)}_{R^{-1}}$ and $\bar{E}^{(2)}_{\exp(-R)}$ have the same sign$^{17}$
while the exact results $E^{(2)}_{R^{-1}}$ and $E^{(2)}_{\exp(-R)}$ have different
signs$^{40}$. This example points out a difficulty with Unsöld's
approximation if the same average energy, $\Delta$, is chosen for the
Fig. (2.3-6) A comparison of various partial sums of the expanded second order energy with the non-expanded second order energy as a function of R for the H(1s)-H+ interaction using exact results. (a) $S(\omega)/E_{R-1}^{(2)}$ (b) $S(\omega)/E^{(2)}$. The value of $\omega$ is indicated on the graph.
\( \tilde{E}_{R-1} \) and \( \tilde{E}_{\exp(-R)} \) parts of \( \tilde{E}^{(2)} \). This is the case, for example, when \( \Delta \) is determined in the usual way\(^{17,46,47}\) by requiring the exact long-range results when charge overlap effects are neglected. This approach would incorporate charge overlap effects properly within \( \tilde{E}_{R-1}^{(2)} \) but could misrepresent the effect of \( \tilde{E}_{\exp(-R)}^{(2)} \) for interactions like \( \text{H}(1s) - \text{H}^+ \) where \( \tilde{E}_{\exp(-R)}^{(2)} \) has the incorrect sign. Kreek\(^{47}\) has investigated the importance of taking this difficulty into account in the choice of \( \Delta \) for the \( \text{H}(1s) - \text{H}^+ \) and the \( \text{H}(1s) - \text{H}(1s) \) interactions including exchange as well as charge overlap effects. The results of his calculations show that this correction does not yield a significant improvement in both cases.

2.4 PADÉ APPROXIMATION METHODS APPLIED TO THE INTERMOLECULAR FORCE SERIES

In this section the possibility of using Padé approximation methods\(^{19,20,61}\) to remove some of the convergence difficulties associated with the direct use of the \( R^{-1} \) expansion of the interaction energy is investigated. The \( \text{H}(1s) - \text{H}^+ \), \( \text{He-He} \), \( \text{H}(1s) - \text{H}(1s) \) and \( \text{H}(1s) - \text{H}(2s) \) interactions are considered as model systems for this purpose. Various Padé approximants and partial sums of the \( R^{-1} \) expansions of the second-order Coulomb interaction energies are
compared with the corresponding non-expanded results for each interaction. The computations are based on the Unsöld's average energy calculations for all four interactions and on exact results for the H(1s)-H⁺ interaction discussed previously.

2.4A  PADÉ APPROXIMANTS

The Padé approximation method has been used successfully to sum a slowly convergent or divergent series in many physical problems. The motivation of this summation method is to obtain an efficient way to extract quantitative information about a function from its power series expansion. The method is to construct rational approximations, from the coefficients of the power series, which represent the function more accurately than the power series itself.

In order to discuss Padé approximation methods for summing the R⁻¹ power series of the second order interaction energies in the Unsöld's approximation for the H(1s)-H⁺, He-He, H(1s)-H(1s) and H(1s)-H(2s) interactions, it is convenient to write Eq. (2.3-13) in the form

\[
\lim_{R \to \infty} l_i m. \tilde{\varepsilon}^{(2)} = - X^K \sum_{n=0}^{\infty} \tilde{C}_{2(n+K)}^{(2)} X^n
\]

(2.4-1)
where $X = R^{-2}$. The $[\tilde{N},\tilde{M}]$ Padé approximant corresponding to Eq. (2.4-1) is then given by

$$\left[ \tilde{N}, \tilde{M} \right] = -X^k P_M(X) / Q_N(X) \quad (2.4-2)$$

where

$$P_M(X) = \sum_{i=0}^{M} p_i X^i, \quad Q_N(X) = 1 + \sum_{i=1}^{N} q_i X^i \quad (2.4-3)$$

The $(M+1)$ coefficients $p_i$ and the $N$ coefficients $q_i$ are obtained by requiring that the power series expansion of Eq. (2.4-2), in the variable $X = R^{-2}$, equal Eq. (2.4-1) term by term through order $(N+M+K)$. This requirement yields a system of $(M+N+1)$ linear equations which can be solved for the $p_i$'s and $q_i$'s;

$$p_i = \sum_{j=0}^{N} \tilde{C}^{(2)}_{2(K+i-j)} q_j \quad ; \quad i = 0, 1, 2, \ldots, M. \quad (2.4-4)$$

$$- \tilde{C}^{(2)}_{2(K+M+1)} = \sum_{j=1}^{N} \tilde{C}^{(2)}_{2(K+M+i-j)} q_j \quad ; \quad i = 1, 2, \ldots, N.$$

where $q_0 = 1$ and $\tilde{C}^{(2)}_{\ell} = 0$ for $\ell < 2K$. Solutions for $p_i$'s and $q_i$'s in terms of the coefficients, $\tilde{C}^{(2)}_{2(\ell+N+K)}$, are given in Table (2.4-1) for various $[\tilde{N},\tilde{M}]$ Padé approximants used in this work. It is clear that in order to obtain a $[\tilde{N},\tilde{M}]$
Table (2.4-1) Values of $p_i$ and $q_i$ of Eq. (2.4-3), $i \geq 1$, given in terms of the coefficients of the power series, $\sum_{n=0}^{\infty} \tilde{c}_i^{(2)} (n+K)x^n$, for various Padé approximants. Here $p_0 = \tilde{c}_2^{(2)}$ and $q_0 = 1$ for all Padé approximants.

<table>
<thead>
<tr>
<th>Padé</th>
<th>$q_1$</th>
<th>$p_1$</th>
<th>$q_2$</th>
<th>$p_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[1,0]$</td>
<td>$-\frac{\tilde{c}_2^{(2)}}{p_0}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$[1,1]$</td>
<td>$\frac{\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}}$</td>
<td>$\tilde{c}_2^{(2)}+p_0q_1$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$[2,1]$</td>
<td>$\frac{\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}} - \frac{\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}}$</td>
<td>$\tilde{c}_2^{(2)}+p_0q_1 - \frac{\tilde{c}_2^{(2)}+\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}}$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$[2,2]$</td>
<td>$\frac{\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}} - \frac{\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}}$</td>
<td>$\tilde{c}_2^{(2)}+p_0q_1 - \frac{\tilde{c}_2^{(2)}+\tilde{c}_2^{(2)}}{\tilde{c}_2^{(2)}}$</td>
<td>$\tilde{c}_2^{(2)}+\tilde{c}_2^{(2)}+p_0q_2$</td>
<td></td>
</tr>
</tbody>
</table>
Padé approximant for $\tilde{E}^{(2)}$ we need to know the first $(N+M+1)$
terms in Eq. (2.4-1) and for notational convenience we
rewrite the truncated series, Eq. (2.3-16), in the form

$$\tilde{S}(\omega) = -X^k \sum_{n=0} S^{(2)}_{2(n+K)} X^n, \quad \omega = N + M$$ \hspace{1cm} (2.4-5)

as the partial sum corresponding to the $[N, M]$ Padé approx-
iment of $E^{(2)}$. An entirely analogous analysis can be made
for Eq. (2.3-22), for the exact $H(1s)-H^+$ results, where
one replaces $\tilde{E}^{(2)}$, $C_{2(n+K)}^{(2)}$, $[N, M]$ and $S(\omega)$ by $E^{(2)}$,
$C_{2(n+K)}^{(2)}$, $[N, M]$ and $S(\omega)$ respectively.

According to practical experience, for a constant
value of $\omega$, the most accurate Padé approximants for a
function are the $[N, N]$ and $[N, N-1]$ approximants. Also
since the polynomials $P_M(X)$ and $Q_N(X)$ may not have the
same sign for certain values of $X$, the Padé approximant,
Eq. (2.4-2), may differ in sign with respect to $E^{(2)}$.
If this occurs the Padé is said to be not available for the
given values of $X$ for the purpose of this work.

2.4B RESULTS AND DISCUSSIONS

In previous sections the $R^{-1}$ expansions have been
shown to be asymptotic to $E^{(2)}_{R^{-1}}$ and not to the total non-
expanded second order energy, $\tilde{E}^{(2)}$. Hence the Padé approx-
imants derived from the $R^{-1}$ expansions are rigorous approx-
imations to \( \tilde{E}^{(2)} \) only when \( \tilde{E}_{R-1}^{(2)} \) is considerably greater in magnitude than \( \tilde{E}_{\exp(-R)}^{(2)} \).

In Figs. (2.4-1)-(2.4-4) ratios of the form 
\[
[\tilde{S}(\omega)/\tilde{E}^{(2)}], \ [\tilde{S}(\omega)/\tilde{E}_{R-1}^{(2)}], \ ([N\tilde{M}]/\tilde{E}_{R-1}^{(2)}) \text{ and } ([N\tilde{M}]/\tilde{E}_{R-1}^{(2)}) \text{ are plotted as a function of } R \text{ for the } H(1s)-H^+ \text{, He-He, } H(1s)-H(1s) \text{ and } H(1s)-H(2s) \text{ interactions in the Unsöld's approximation. The graphs involving } [N\tilde{M}] \text{ are truncated as a function of decreasing } R \text{ at the value of } R \text{ where } [N\tilde{M}] \text{ differs in sign with respect to } \tilde{E}_{R-1}^{(2)} \text{ or } \tilde{E}^{(2)}; \text{ see Sec. 2.4A.}
\]

In all cases, for values of \( R \) where the \( R^{-1} \) expansions have meaning (see Sec. 2.3B), the Padé approximants as well as the partial \( R^{-1} \) sums represent \( \tilde{E}_{R-1}^{(2)} \) more accurately than \( \tilde{E}^{(2)} \) and each Padé approximant gives better representations of \( \tilde{E}_{R-1}^{(2)} \) or \( \tilde{E}^{(2)} \) than the corresponding partial sum, see Figs. (2.4-1)-(2.4-4). For large values of \( R \) better approximations can be generated by using Padé approximates (or partial sums) corresponding to larger values of \( (N+M) \) or \( \omega \). However the larger \( (N+M) \) or \( \omega \) the more rapid is the divergence from the non-expanded results as \( R \) decreases in value. It should be emphasized that for large values of \( (N+M) \) or \( \omega \) the Padé approximant often yields only a trivial improvement over the results obtained by using the corresponding partial sum. For example, the improvement in using the approximants \([2\tilde{\omega},1]\) and \([2\tilde{\omega},2]\) is not visible.
Fig. (2.4-1) A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of \( R \) for the \( \text{H}(1s) - \text{H}^+ \) interaction in Unsöld's approximation. (a) \( \tilde{S}(\omega) / \tilde{E}_{R-1}^{(2)} \) and \( [N,M] / \tilde{E}_{R-1}^{(2)} \). (b) \( \tilde{S}(\omega) / \tilde{E}^{(2)} \) and \( [N,M] / \tilde{E}^{(2)} \). The values of \( \omega \) and \([N,M]\) are indicated on the graph.
Fig. (2.4-2) A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the He-He interaction in Unsöld's approximation. (a) $\tilde{S}(\omega)/E_R^{(2)}$ and $[N_{\tilde{M}}]/E_R^{(2)}$ (b) $\tilde{S}(\omega)/E_R^{(2)}$ and $[N_{\tilde{M}}]/E_R^{(2)}$. The values of $\omega$ and $[N_{\tilde{M}}]$ are indicated on the graph.
Fig. (2.4-3) A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $H(1s)$-$H(1s)$ interaction in Unsöld's approximation.

(a) $\tilde{S}(\omega)/E_{R-1}^{(2)}$ and $[N, M]/E_{R-1}^{(2)}$ (b) $\tilde{S}(\omega)/E^{(2)}$ and $[N, M]/E^{(2)}$. The values of $\omega$ and $[N, M]$ are indicated on the graph.
Fig. (2.4-4) A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $H(1s)-H(2s)$ interaction in Unsöld's approximation. (a) $\tilde{S}(\omega)/\tilde{E}^{(2)}_R$ and $[\tilde{N},\tilde{M}]/\tilde{E}^{(2)}_R$ (b) $\tilde{S}(\omega)/\tilde{E}^{(2)}$ and $[\tilde{N},\tilde{M}]/\tilde{E}^{(2)}$. The values of $\omega$ and $[\tilde{N},\tilde{M}]$ are indicated on the graph.
using the scale of part (a) of Figs. (2.4-1)-(2.4-4).

These results (see also below) show that the Padé technique can accelerate the convergence of the $R^{-1}$ expansions for values of $R$ where the expansions are meaningful. This is particularly the case for interactions involving excited or larger species where the slow rate of convergence of the $R^{-1}$ series is more noticeable; see Fig. (2.4-4) and consider the $[1,0]$ Padé for example. For the $H(1s)-H(2s)$ interaction the $[1,0]$ Padé approximant, based on the two-term partial sum $\tilde{S}(1)$, gives a more accurate representation of $\tilde{E}^{(2)}_{R^{-1}}$ than the three-term partial sum $\tilde{S}(2)$ and represents $\tilde{E}^{(2)}$ about as well as the four-term partial sum $\tilde{S}(3)$. Numerically for example at $R = 18 \ a_0$, the partial sums $\tilde{S}(1), \tilde{S}(2)$ and the Padé $[1,0]$, respectively, are in error by approximately 18, 11 and 8 per cent as a representation of $\tilde{E}^{(2)}_{R^{-1}}$ and are in error by about 33, 24 and 23 per cent as a representation of $\tilde{E}^{(2)}$ itself.

The Padé approximants to the exact results for the $H(1s)-H^+$ interaction have also been calculated. In Fig. (2.4-5) graphs analogous to Fig. (2.4-1) are plotted for the exact $H(1s)-H^+$ results. The trends, as far as the Padé approximants are concerned, are very similar to the Unsöld's results for the $H(1s)-H^+$ interaction. The reason for the marked difference between Figs. (2.4-5b) and (2.4-1b) has
Fig. (2.4-5) A comparison of various partial sums and Padé approximants of the expanded second order energy with the non-expanded second order energy as a function of $R$ for the $\text{H}(1s) - \text{H}^+$ interaction using exact results. (a) $S(\omega)/E_{R-1}^{(2)}$ and $[N,M]/E_{R-1}^{(2)}$ (b) $S(\omega)/E^{(2)}$ and $[N,M]/E^{(2)}$. The values of $\omega$ and $[N,M]$ are indicated on the graph.
been discussed in Sec. 2.3C.

Finally it should be emphasized that there are several ways to attempt to improve the convergence of the $R^{-1}$ expansions of the intermolecular energies. One method suggested by Dalgarno and Lewis is to truncate the $R^{-1}$ expansions by summing them to one-half their smallest term as a function of $R$. This approach yields useful representations of $\tilde{E}_R^{(2)}$ and $\tilde{E}^{(2)}$ but has the disadvantage that often many of $R^{-1}$ energies are required to obtain reasonable results. In Table (2.4-2) results obtained by using this truncation scheme are given for the $\text{H(1s)-H}^+$, $\text{He-He}$, $\text{H(1s)-H(1s)}$ and $\text{H(1s)-H(2s)}$ interactions in the Unsöld's approximation. For example, for the $\text{H(1s)-H(2s)}$ interaction at $R = 18$ a$_0$ six terms are required to obtain a result for $\tilde{E}^{(2)}$ comparable to the $[1,1]$ Padé which requires only three terms [see Fig. (2.4-4b)]. For the $\text{H(1s)-H}^+$ interaction at $R = 6$ a$_0$ five terms are required to obtain a result comparable to the $[1,1]$ Padé [see Fig. (2.4-1b)]. It is clear that the use of this truncation scheme, as well as the direct use of the $R^{-1}$ series, is severely limited since in most practical applications only first few terms in the $R^{-1}$ expansions are known with any degree of accuracy for most interactions. In such circumstances the Padé approximant method appears to be a simple useful way to remove some of
Table (2.4-2) Results of summing $R^{-1}$ series in Unsöld's approximation, by the method of Dalgarno and Lewis, for various interactions.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$H(1s)-H^+$</th>
<th>He-He</th>
<th>$H(1s)-H(1s)$</th>
<th>$H(1s)-H(2s)\Sigma_g^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td># of terms</td>
<td>% of $\sim E^{(2)}$</td>
<td># of terms</td>
<td>% of $\sim E^{(2)}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>88</td>
<td>1</td>
<td>219</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>95</td>
<td>4</td>
<td>79</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>99</td>
<td>7</td>
<td>99</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>100</td>
<td>11</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>100</td>
<td>14</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
the difficulties associated with the slow rate of convergence of the $R^{-1}$ series representation of the interaction energy. However, it does not alleviate the problems associated with the asymptotic divergent nature of the series. This is not unreasonable since $R^{-1}$ is not a good expansion parameter for the interaction energy for "small" values of $R$. Indeed the Padé approximants probably give a more realistic indication of the asymptotic nature of the intermolecular force series than the corresponding $R^{-1}$ partial sums.
3. GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY

CALCULATIONS OF INTERMOLECULAR FORCES INCLUDING

EXCHANGE EFFECTS

Rayleigh-Schrödinger perturbation theory is useful in the study of intermolecular forces if the electron exchange effects between the two interacting species are negligible so that the Hamiltonian for the whole system can be decomposed into a zeroth Hamiltonian $H_0$ and a perturbation potential energy $V$; see Sec. 2.1. However if the electron exchange effects between the two species are not neglected there is in general no convenient way of choosing $H_0$ and other perturbation methods\textsuperscript{67-71} must be used to calculate the interaction energy. One of the perturbation theories which does not require the decomposition of the total Hamiltonian into a zeroth Hamiltonian and a perturbation potential energy is the generalized Brillouin-Wigner perturbation theory\textsuperscript{21,22,72,73}. In this theory, calculations

\textsuperscript{\#}In the case where the wavefunction can be separated into spatial and spin parts, the Sternheimer technique\textsuperscript{9} can be used to treat\textsuperscript{76-78} the problem with exchange in the Rayleigh-Schrödinger theory.

61
beyond first order in the energy are very difficult due to
the evaluation of matrix elements over a complete set of
basis functions. This is especially true when exchange
effects are included in the calculations. The calculations
through second order in energy can be greatly simplified
by the application of Unsöld's approximation \(^{42}\) to the
second order energy \(^{46,47,74}\). However this treatment still
involves a very considerable computational task in the
evaluation of matrix elements involving the square of the
Hamiltonian, see below. Also the application of the method to
the third order energy leads to divergent results \(^{30,75}\) for
ground states.

In this chapter the Brillouin-Wigner perturbation theory
in the Unsöld's approximation, will be modified to avoid the
difficulties in evaluating the matrix elements of the square
and cube of the Hamiltonian. This modified treatment is
then used to calculate the interaction energies through
second order between two hydrogen atoms in various states
for intermediate internuclear separations where the charge
overlap effects (see Chapter 2) and the exchange effects
are both appreciable. The calculated results are compared
with the corresponding exact results, when available, to
provide detailed discussions on the usefulness of this approx-
imate perturbation method.
3.1 GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY

The Generalized Brillouin-Wigner perturbation theory developed by Brillouin\(^2\) and Wigner\(^2\), see also Lennard-Jones\(^7\), is derived briefly here using a modification of the original treatment as proposed by Feenberg\(^7\); see also Löwdin\(^7\). The derivation here is similar to that given in Ref. (10). The general results are simplified by introducing the Unsöld's average energy approximation into the formalism and by using a modified Hamiltonian \( \hat{H} \) to avoid the necessity of calculating the matrix elements of the square and cube of the Hamiltonian.

3.1A GENERAL THEORY\(^1\)

The exact wavefunction \( \Psi \) for the system of interest is expanded in terms of a complete and general set of functions \( \{ \chi_j \} \):

\[
\Psi = \chi_0 + \sum_{j=1}^{\infty} C_j \chi_j \quad (3.1-1)
\]

in which \( \chi_0 \) resembles \( \Psi \) as closely as conveniently possible. \( \Psi \) satisfies the Schrödinger equation

\[
(\hat{H} - E) \Psi = 0 \quad (3.1-2)
\]

Substituting Eq. (3.1-1) into (3.1-2) one obtains, after some straightforward manipulations;
\[ C_j = -\frac{H_{j\alpha} - ES_{j\alpha}}{H_{jj} - ES_{jj}} - \sum_{k \neq \alpha} \frac{C_k (H_{jk} - ES_{jk})}{H_{jj} - ES_{jj}} \]  

where

\[ H_{ij} = \langle \chi_i | H | \chi_j \rangle, \quad S_{ij} = \langle \chi_i | \chi_j \rangle. \]

The energy perturbation expansion is given by

\[ E = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} + \mathcal{E}^{(2)} + \mathcal{E}^{(3)} + \mathcal{E}^{(3)}(\text{Re}) \]

where

\[ \mathcal{E}^{(0)} + \mathcal{E}^{(1)} = \frac{H_{oo}}{S_{oo}} \]

\[ \mathcal{E}^{(2)} = -\sum_{j \neq o} \frac{|H_{oj} - ES_{oj}|^2}{(H_{jj} - ES_{jj})S_{oo}} \]

\[ \mathcal{E}^{(3)} = \sum_{j \neq o} \sum_{k \neq o} \frac{(H_{oj} - ES_{oj})(H_{jk} - ES_{jk})(H_{ko} - ES_{ko})}{(H_{jj} - ES_{jj})(H_{kk} - ES_{kk})S_{oo}} \]

and

\[ \mathcal{E}^{(3)}(\text{Re}) = \sum_{j \neq o} \sum_{k \neq o} \sum_{l \neq o, k} \frac{C_l (H_{oj} - ES_{oj})(H_{jk} - ES_{jk})(H_{ko} - ES_{ko})}{(H_{jj} - ES_{jj})(H_{kk} - ES_{kk})S_{oo}}. \]
By substituting $C_k$ from Eq. (3.1-3) into the remainder $\varepsilon^{(3)}(\text{Re})$, a "fourth order" term plus a new remainder $\varepsilon^{(4)}(\text{Re})$ is obtained. The higher order energy terms can be obtained by continued repetition of this procedure.

Substituting Eq. (3.1-3) into Eq. (3.1-1) yields

$$
\Psi = \chi_0 - \sum_{j \neq 0} \frac{(H_{j^0} - E S_{j^0})}{(H_{j^0} - E S_{j^0})} \chi_j - \sum_{j \neq 0} \sum_{k \neq 0} \frac{C_k (H_{j^k} - E S_{j^k})}{(H_{j^k} - E S_{j^k})} \chi_j. \tag{3.1-10}
$$

If one identifies the 1st order generalized Brillouin-Wigner wavefunction as

$$
\psi^{(1)} = - \sum_{j \neq 0} \frac{(H_{j^0} - E S_{j^0})}{(H_{j^0} - E S_{j^0})} \chi_j \tag{3.1-11}
$$

one can write Eq. (3.1-10) as

$$
\Psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)}(\text{Re}) \tag{3.1-12}
$$

where $\psi^{(0)} = \chi_0$ is the zeroth order generalized Brillouin-Wigner wavefunction. Substituting $C_k$ from Eq. (3.1-3) into Eq. (3.1-10) yields the second order generalized Brillouin-Wigner wavefunction and a new remainder $\psi^{(2)}(\text{Re})$. The higher order generalized Brillouin-Wigner wavefunctions can be obtained by repetition of this procedure.
The energies \( \varepsilon^{(2)} \) and \( \varepsilon^{(3)} \) can be written in the form

\[
\varepsilon^{(2)} = \langle \Psi^{(0)} | H - E | \Psi^{(0)} \rangle \\
\varepsilon^{(3)} = \langle \Psi^{(0)} | H - E | \Psi^{(0)} \rangle + \varepsilon^{(2)}
\]

(3.1-13)

(3.1-14)

with the condition,

\[
S_{oo} = 1
\]

(3.1-15)

At first glance Eq. (3.1-14) looks peculiar because it contains the second order energy. However if one substitutes Eqs. (3.1-11) and (3.1-7) into Eq. (3.1-14), the second order energy cancels and one recovers Eq. (3.1-8).

The perturbation expansion of the energy through third order, Eq. (3.1-5), is an upper bound\(^{22,74}\) to the exact energy \( E \). If one calculates the expectation value of the Hamiltonian\(^{80}\),

\[
\frac{\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E
\]

(3.1-16)

using the trial wavefunction

\[
\tilde{\Psi} = \Psi^{(o)} + \Psi^{(n)}
\]

(3.1-17)

it is easy to show that
\[ \mathcal{E}^{(0)} + \mathcal{E}^{(n)} + \mathcal{E}^{(2)} + \mathcal{E}^{(3)} \geq E \quad . \quad (3.1-18) \]

Indeed the energy through \((2n+1)\) order obtained from the generalized Brillouin-Wigner perturbation theory is an upper bound\(^{22,74}\) to the exact energy, \(E\). This is easily shown by calculating the expectation value of the Hamiltonian, Eq. \((3.1-16)\), using a generalized Brillouin-Wigner wavefunction through \(n\)-th order as the trial wavefunction.

3.1B UNSÖLD'S APPROXIMATION FOR THE GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY

The Unsöld's approximation has been used in Sec. 2.2 to simplify the calculations of the second order energy in the Rayleigh-Schrödinger perturbation theory. Here it is used to simplify the calculations of the second order energy, \(\mathcal{E}^{(2)}\), in the generalized Brillouin-Wigner perturbation theory\(^46,47,81\).

Let us apply the Unsöld's approximation to Eq. \((3.1-11)\) or Eq. \((3.1-7)\) with \(S_{00} = 1\). The denominator, \(H_{jj} - ES_{jj}\), is assumed to be a constant, \(\Delta\), independent of the index \(j\). One obtains, by making use of the matrix sum rule,

\[ \psi^{(\omega)} \rightarrow \tilde{\psi}^{(\omega)} = - \Delta' \left\{ H - H_{\omega} \right\} \psi^{(\omega)} \quad (3.1-19) \]
\[ \mathcal{E}^{(2)} \rightarrow \tilde{\mathcal{E}}^{(2)} = -\Delta^{-1} \left\{ \langle \psi^{(o)} | H^2 | \psi^{(o)} \rangle - (H_{oo})^2 \right\} \]  

(3.1-20)

Here, \( \mathcal{E}^{(2)} \) can also be obtained by substituting Eq. (3.1-19) into Eq. (3.1-13). Substituting Eq. (3.1-19) into Eq. (3.1-14) and using Eq. (3.1-20) for \( \mathcal{E}^{(2)} \) one can show that the Unsöld's approximation for the third order energy is given by

\[ \mathcal{E}^{(3)} \rightarrow \tilde{\mathcal{E}}^{(3)} = \Delta^2 \left\{ \langle \psi^{(o)} | H^3 | \psi^{(o)} \rangle - 2H_{oo} \langle \psi^{(o)} | H^2 | \psi^{(o)} \rangle + H_{oo}^3 - E \langle \psi^{(o)} | H^2 | \psi^{(o)} \rangle + E H_{oo}^2 \right\} + \mathcal{E}^{(2)}. \]  

(3.1-21)

The third order energy can also be obtained directly from Eq. (3.1-8) by assuming the quantities \( (H_{kk} - ES_{kk}) \) and \( (H_{jj} - ES_{jj}) \) are constants, \( \Delta' \) and \( \Delta'' \), respectively. In this case the results for \( \tilde{\mathcal{E}}^{(3)} \) will have \( (\Delta' \Delta'')^{-1} \) instead of \( \Delta^{-2} \) in Eq. (3.1-21).

The energy through third order can be shown to be an upper bound to the exact energy,

\[ \mathcal{E}^{(o)} + \mathcal{E}^{(1)} + \tilde{\mathcal{E}}^{(2)} + \tilde{\mathcal{E}}^{(3)} \geq E \]  

(3.1-22)

if one uses the trial wavefunction,
\( \bar{\psi} = \psi^{(o)} + \bar{\psi}^{(i)} \) \hspace{1cm} (3.1-23)

in Eq. (3.1-16). It should be pointed out that (3.1-22) holds only if \( \Delta' \) and \( \Delta'' \) are chosen to be equal to \( \Delta \).

3.1C MODIFICATION OF THE GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY IN THE UNSÖLD'S APPROXIMATION

The second order energy in the Unsöld's approximation, \( \bar{\varepsilon}^{(2)} \), is hard to calculate because it is difficult to evaluate the matrix elements of the square of the Hamiltonian, \( H^2 \), see Eq. (3.1-20). In order to eliminate this difficulty one can modify the theory by modifying the Hamiltonian occurring in Eq. (3.1-19) to yield

\[
\bar{\psi}^{(i)} \rightarrow \bar{\psi}^{(i)} = -\Delta' \left( \bar{H} - \bar{H}_{oo} \right) \psi^{(o)}
\]  \hspace{1cm} (3.1-24)

where

\[
\bar{H}_{oo} = \langle \psi^{(o)} \mid \bar{H} \mid \psi^{(o)} \rangle
\]  \hspace{1cm} (3.1-25)

\( \bar{H} \) is the modified Hamiltonian chosen to simplify the evaluation of the matrix elements of \( H^2 \) and will be defined later. Substituting Eq. (3.1-24) into Eq. (3.1-13) one obtains, after some simple manipulations,
\[
\bar{\mathcal{E}}^{(2)} \rightarrow \bar{\mathcal{E}}^{(2)} = - \Delta^{-1} \left\{ \langle \Psi^{(0)} | \bar{H} \bar{H} - \bar{H}_o \bar{H}_o | \Psi^{(0)} \rangle \right\} .
\] 

It should be pointed out here that this general treatment is analogous to that discussed by Margenau\textsuperscript{81} and Slater and Kirkwood\textsuperscript{82} for the treatment of intermolecular forces, see also Sec. 3.2 and Ref. (32).

The third order energy in the Unsöld's approximation, \(\bar{\mathcal{E}}^{(3)}\), is extremely difficult to evaluate because it contains the matrix element of \(\bar{H}^3\). Indeed for the ground state molecule the matrix element of \(\bar{H}^3\) diverges\textsuperscript{30,75}. These difficulties are also eliminated by the introduction of the modified Hamiltonian. That is, substituting Eq. (3.1-24) into Eq. (3.1-14) one obtains

\[
\bar{\mathcal{E}}^{(3)} \rightarrow \mathcal{E}^{(3)} = \Delta^2 \left\{ \langle \Psi^{(0)} | \bar{H} \bar{H} \bar{H} | \Psi^{(0)} \rangle - \mathcal{E} \langle \Psi^{(0)} | \bar{H}^2 | \Psi^{(0)} \rangle \\
- 2 \bar{H}_o \langle \Psi^{(0)} | \bar{H} \bar{H} | \Psi^{(0)} \rangle + \mathcal{E} \bar{H}_o^2 + \bar{H}_o \bar{H}_o \bar{H}_o \right\} + \bar{\mathcal{E}}^{(2)} .
\] 

Eq. (3.1-26) and (3.1-27) are similar in form to Eqs. (3.1-20) and (3.1-21) respectively. If one replaces \(\bar{H}\) by \(H\) in Eqs. (3.1-26) and (3.1-27) one recovers Eqs. (3.1-20) and (3.1-21).
The energy, \( (\varepsilon^{(0)} + \varepsilon^{(1)} + \varepsilon^{(2)} + \varepsilon^{(3)}) \), can also be shown to be an upper bound to the exact energy, \( E \); it is the expectation value of the Hamiltonian obtained by using the trial wavefunction,

\[
\tilde{\Psi} = \Psi^{(0)} + \Psi^{(1)}
\]  

(3.1-28)

3.2 APPLICATION OF THE MODIFIED BRILLOUIN-WIGNER PERTURBATION THEORY IN UNSÖLD'S APPROXIMATION TO INTERMOLECULAR FORCES

In this section the perturbation theory discussed in Sec. 3.1 is applied to the calculation of intermolecular forces. Here the zeroth order wavefunction, \( \Psi^{(0)} \), is taken to be the antisymmetrized product of the exact wavefunctions for the isolated species or a linear combination of these antisymmetrized products; see for example Ref. (39a). Thus \( \Psi^{(0)} \) is expressed in the form

\[
\Psi^{(0)} = NA_{ab} \Psi^{(0)}
\]  

(3.2-1)

where \( N \) is a normalization constant, \( A_{ab} \) is the antisymmetrizer \( 32,83-85 \) for the exchange of electrons between the interacting species "a" and "b" and \( \Psi^{(0)} \) is the zeroth order wavefunction used in the Rayleigh-Schrödinger treat-
ment of long range intermolecular forces discussed in Sec. 2.1; see Eqs. (2.1-19) and (2.1-26).

If electron exchange effects are neglected between species "a" and "b", the Hamiltonian for the system can be written, see Eq. (2.1-2), as

\[ H = H_0 + V \]  \hspace{1cm} (3.2-2)

where \( H_0 \) and \( V \) are, respectively, the zeroth Hamiltonian and the potential energy corresponding to \( \Psi^{(0)} \). The modified Hamiltonian \( \overline{H} \) used in this work is obtained from Eq. (3.2-2) by modifying \( V \),

\[ \overline{H} = H_0 + \overline{V} \]  \hspace{1cm} (3.2-3)

where \( \overline{V} \) represents the modified \( V \), see below.

Substituting Eq. (3.2-1) into Eqs. (3.1-24) and (3.1-26) and using the following identities \(^{83,86}\),

\[ [\overline{H}, A_{ab}] = [H, A_{ab}] = 0 \]

\[ \overline{H} \Psi^{(0)} = (H_0 + \overline{V}) \Psi^{(0)} = (\mathcal{E}^{(0)} + \overline{V}) \Psi^{(0)} \]

\[ H \Psi^{(0)} = (H_0 + V) \Psi^{(0)} = (\mathcal{E}^{(0)} + V) \Psi^{(0)} \]  \hspace{1cm} (3.2-4)
\[ \bar{H}_{oo} = \mathcal{E}^{(o)} + \bar{\mathcal{E}}^{(i)} = \mathcal{E}^{(o)} + \bar{\mathcal{E}}^{(i)} \]

\[ \bar{\mathcal{E}}^{(i)} = N^2 \left< A_{ab}^2 \Psi^{(o)} | \nabla \Psi^{(o)} \right> \]

\[ \mathcal{E}^{(i)} = N^2 \left< A_{ab}^2 (\nabla \Psi^{(o)}) | \Psi^{(o)} \right> \]

one obtains

\[ \bar{\Psi}^{(o)} = - \frac{N}{\Delta} A_{ab} \left\{ (\bar{\nabla} - \bar{\mathcal{E}}^{(i)}) \Psi^{(o)} \right\} \] \( (3.2-5) \)

and

\[ \bar{\mathcal{E}}^{(2)} = - \frac{N^2}{\Delta} \left\{ \left< A_{ab}^2 (\nabla \Psi^{(o)}) | \nabla \Psi^{(o)} \right> - \mathcal{E}^{(i)} \bar{\mathcal{E}}^{(o)} \right\} \] \( (3.2-6) \)

The results of Eq. (3.2-6) can also be obtained by substituting Eqs. (3.2-1) and (3.2-5) into Eq. (3.1-13) for \( \bar{\mathcal{E}}^{(2)} \).

Similar results can be obtained for \( \bar{\mathcal{E}}^{(3)} \) by substituting Eq. (3.2-1) into Eq. (3.1-27) or by substituting Eq. (3.2-5) into Eq. (3.1-14). The results for \( \bar{\mathcal{E}}^{(3)} \) are complicated and will not be shown here since in this work the energy is calculated only through second order.

Using Eq. (3.2-5) for \( \psi^{(1)} \) in Eq. (3.1-12) one obtains
the modified generalized Brillouin-Wigner wavefunction through first order in the form

$$\Psi = \Psi^{(0)} + \bar{\Psi}^{(0)} = N A_{ab} \left\{ \left[ 1 - \frac{1}{\xi} (\bar{V} - \bar{E}^{(0)}) \right] \Psi^{(0)} \right\}$$  \hspace{1cm} (3.2-7)

This wavefunction is analogous to the variational wavefunction used by Margenau$^{32,81}$ to incorporate exchange effects into treatments of the H–H and the He–He interactions; see also Hasse$^{87}$, Slater and Kirkwood$^{82}$, Hirschfelder and Linnett$^{88}$ and Moore$^{89}$.

The interaction energy through second order in the modified Unsöld's approximate generalized Brillouin-Wigner perturbation theory is given by

$$\bar{E}_{ab} = E^{(0)} + \bar{E}^{(0)} + \bar{E}^{(2)} - E^{(0)} = E^{(0)} + \bar{E}^{(2)}$$  \hspace{1cm} (3.2-8)

where $E^{(0)} = \bar{E}^{(0)}$ is the energy for the two isolated species.
3.3 APPLICATION OF THE MODIFIED UNSÖLD'S APPROXIMATE GENERALIZED BRILLOUIN-WIGNER PERTURBATION THEORY TO SOME H(1s)–H(n=2) INTERACTIONS

In this section the interaction energies for the H–H interactions that lead to the hydrogen molecular states, \( X^1\Sigma_g^+(1s,1s) \), \( \beta^3\Sigma_u^+(1s,1s) \), \( a^3\Sigma_g^+(1s,2p \sigma) \), \( C^1\Pi_u(1s,2p \pi) \), \( ^3\Pi_g(1s,2p \pi) \), \( ^1\Pi_g(1s,2p \pi) \), and \( ^3\Pi_u(1s,2p \pi) \), are calculated for \( R = 2(2)16 \) a₀ by using the perturbation method discussed in Secs. 3.1C and 3.2. The results obtained are compared with the corresponding exact results\(^{90,91}\) to provide detailed discussions on the usefulness of this approximate perturbation method. The \( ^3\Sigma_g^+(1s,2s) \), \( ^1\Sigma_g^+(1s,2s) \), \( ^1\Sigma_u^+(1s,2p \sigma) \), \( ^1\Sigma_u^+(1s,2p \pi) \), \( ^3\Sigma_u^+(1s,2p \sigma) \) and \( ^3\Sigma_u^+(1s,2p \pi) \) states are not considered in this work because these states either involve ionic terms in their wavefunctions\(^{39a,92-95}\) which complicate the calculations\(^\dagger\) or correspond to states for which accurate results are not

\[\dagger\] The purpose of the present calculations is to test the feasibility of using the approximate perturbation technique to calculate intermediate range intermolecular forces. We deliberately avoid these complicated cases. However it should be noted that the application of this perturbation technique to cases involving ionic terms appears to be straightforward.
available for an appropriate range of \( R \) values\(^ {96,97} \).

Since electron exchange between the two interacting species is considered in this section for the interaction of two hydrogen atoms, the eigenfunctions \( \varphi_a(u) \) and \( \varphi_b(u') \) used in Sec. 2.2 for the discussion of the long range interaction between species "a" and "b" have to be modified to specify explicitly the electrons associated with a given proton "a" or "b". Let \( \varphi_a(n \ell m; i) \) and \( \varphi_b(n \ell m; j) \) be the spatial parts of the hydrogen atom wavefunctions corresponding to protons "a" and "b" with electrons \( i \) and \( j \) respectively; \( i; j = 1,2 \). \( \alpha(i) \) and \( \beta(i) \) are the spin wavefunctions for electron \( i \). The zeroth order wavefunctions, \( \psi^{(0)} \), for the H(1s)–H(n \ell m) interactions can be constructed from valence bond theory\(^ {96} \) using methods similar to that discussed by Mulliken\(^ {39a} \).

In general the wavefunctions corresponding to the states considered here for the H(1s)–H(n \ell m) interactions can be written in the form

\[
\psi^{(0)}(\Lambda_S P) = \left[ 2(1 + s') \right]^{1/2} A_{ab} \left\{ \left[ \psi_a^{(1)} \varphi_b(n \ell m; 2) + \psi_b^{(1)} \varphi_a(n \ell m; 1) \right] s_a \right\} \times \left[ \alpha(1) \beta(2) - \eta \beta(1) \alpha(2) \right] \quad (3.3-1)
\]
where $\Lambda = |M_L|$. Here $M_L$ is the projection of the total electronic orbital angular momentum $L$ of the diatomic molecule on the internuclear axis$^{98-100}$, $S$ is the total electronic spin of the molecule and $\rho$ is the parity, $g$ or $u$, referring to the inversion symmetry of the electronic wavefunction with respect to the internuclear midpoint. For $\Sigma$ states ($\Lambda = 0$), a further symmetry property exists$^{98-100}$, namely the reflection of the wavefunction in any plane through the symmetry axis ($+1$ for $\Sigma^+$, $-1$ for $\Sigma^-$). This is not specified in Eq. (3.3-1) since all $\Sigma$ states considered in this work are $\Sigma^+$ states. The values for the parameters, $\eta$ and $\rho$, corresponding to the states considered here are given in Table (3.3-1) and

$$S' = \left| \langle \Psi_d | \Psi_b (n \ell m ; i) \rangle \right|^2$$

$$+ \gamma \langle \Psi_d (i) | \Psi_b (i) \rangle \langle \Psi_a (n \ell m ; i) | \Psi_b (n \ell m ; i) \rangle \delta_{n,2} \quad (3.3-2)$$

The wavefunctions, corresponding to triplet states, consisting of spin wavefunctions, $\alpha (1) \alpha (2)$ or $\beta (1) \beta (2)$, are not considered here since they are degenerate with the wavefunction given by Eq. (3.3-1) if spin–orbit coupling terms are neglected in the Hamiltonian and there are no external fields$^{39a,86,98-100}$. 
Table (3.3-1) Values for the parameters, $\eta$ and $\rho$, used to specify the wavefunction, Eq. (3.3-1), for various molecular states of H$_2$ considered in Sec. 3.3.

<table>
<thead>
<tr>
<th>States</th>
<th>$\rho$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^1\Sigma_g^+(1s,1s)$</td>
<td>0</td>
<td>+1</td>
</tr>
<tr>
<td>$b^3\Sigma_u^+(1s,1s)$</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$^3\Sigma_g^+(1s,2p_\sigma)$</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>$^3\Sigma_g^+(1s,2s)$</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$C^4\pi_u(1s,2p_\pi)$</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>$^3\pi_g(1s,2p_\pi)$</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>$^1\pi_g(1s,2p_\pi)$</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>$^3\pi_u(1s,2p_\pi)$</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Note: The wavefunction for the $a^3\Sigma_g^+$ state is a linear combination of the two $^3\Sigma_g^+$ functions given in this Table, see text.
It must be pointed out here that due to the degeneracy of the 2s and 2p_{s} states of the hydrogen atom a mixing of the 1s2s and 1s2p_{s} configurations occur^{39a,90b,96} in the calculations for the a^{3}\Sigma_{g}^{+}(1s,2p_{s}) state when charge overlap and exchange effects are not zero, see also Sec. 2.3A. Degenerate perturbation theory^{9,100} must be used to evaluate the first order energy and to find the proper zeroth order wavefunction \psi^{(0)} from the linear combination of the wavefunctions for the two configurations. This is discussed in Appendix E.

For the H(1s)–H(n \ell m) interactions considered here, the Hamiltonian is easily obtained and \vec{V} is given by Eq. (2.3-2). The modified Hamiltonian \vec{\bar{H}} = H_{0} + \vec{\bar{V}} is obtained by using the first two terms of the multipole expansion, Eq. (2.2-2), of the interaction potential energy for \vec{\bar{V}};

\[
\vec{\bar{V}} = V_{3} R^{-3} + V_{4} R^{-4}
\]  

(3.3-3)

The perturbation calculations are carried out through second order for the energy. Substituting Eq. (3.3-3) into Eq. (3.2-6), one obtains the second order energy which can be written in the form
\[ \bar{E}^{(2)} = -\frac{N^2}{\Delta} \left\{ \langle A_{ab}^2 (V \Psi^{(0)}) | V_3 \Psi^{(0)} \rangle - \bar{E}^{(0)} \langle A_{ab}^2 \Psi^{(0)} | V_3 \Psi^{(0)} \rangle R^{-3} 
\right. \\
\left. + \langle A_{ab}^2 (V \Psi^{(0)}) | V_4 \Psi^{(0)} \rangle - \bar{E}^{(0)} \langle A_{ab}^2 \Psi^{(0)} | V_4 \Psi^{(0)} \rangle R^{-4} \right\} \] (3.3-4)

The choice of the Unsöld's average energy, \( \Delta \), in Eq. (3.3-4) depends on the interactions under consideration.

**Case I:** The \( X^1\Sigma_g^+ \) and \( b^3\Sigma_u^+ \) states of \( \text{H}_2 \).

For these states, when charge overlap and exchange effects are neglected (schematically \( \lim R \to \infty \), see Chap. 2), Eq. (3.3-4) can be written in the form,

\[ \lim_{R \to \infty} \bar{E}^{(2)} = -\frac{1}{\Delta} \left\{ \frac{C'_6}{R^6} + \frac{C'_8}{R^8} + \frac{C''_{10}}{R^{10}} + \cdots \right\} \] (3.3-5)

where the \( \frac{C'_m}{\Delta} = \bar{C}^{(2)}_m \), \( m = 6, 8 \), are the "exact" Unsöld's expansion coefficients discussed in Secs. 2.2 and 2.3, see Table (3.3-2). \( \frac{C''_{10}}{\Delta} \) and the coefficients of the higher order terms in \( R^{-1} \) occurring in (3.3-5) represent only part of the Unsöld's expansion coefficients since \( \bar{V} \), Eq. (3.3-3), which has been used to give Eq. (3.3-4), is not the complete multipole expansion for \( V \). The Unsöld's average energy, \( \Delta \), is chosen in the following ways;
Table (3.3-2) Values for the "exact" Unsöld's expansion coefficients, $\tilde{C}_m^{(2)}$, $m = 6, 8$, in units of $\Delta'$, for various states of some $H(1s)-H(n \ell m)$ interactions.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>State</th>
<th>$\tilde{C}_6^{(2)}$</th>
<th>$\tilde{C}_8^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H(1s)-H(1s)$</td>
<td>$X^1\Sigma_g^+, b^3\Sigma_u^+$</td>
<td>6</td>
<td>135</td>
</tr>
<tr>
<td>$H(1s)-H(2p_{\sigma})$</td>
<td>$^1\Sigma_g^+, ^3\Sigma_u^+$</td>
<td>82.77</td>
<td>15004.94</td>
</tr>
<tr>
<td></td>
<td>$^1\Sigma_u^+, ^3\Sigma_g^+$</td>
<td>82.77</td>
<td>15289.06</td>
</tr>
<tr>
<td>$H(1s)-H(2p_{\pi})$</td>
<td>$^1\pi_u^+, ^3\pi_g$</td>
<td>48</td>
<td>5619.24</td>
</tr>
<tr>
<td></td>
<td>$^1\pi_g^+, ^3\pi_u$</td>
<td>48</td>
<td>5434.64</td>
</tr>
</tbody>
</table>
i) $\Delta = \Delta_1$ such that the first term in Eq. (3.3-5) reproduces the exact long range $R^{-6}$ term of the interaction energy.

$$\Delta_1 = + \frac{C'_6}{C_6} \quad (3.3-6)$$

where $C_n$ is the exact coefficient $^{36,56}$ of the $R^{-n}$ expansion for the long range interaction energy.

ii) $\Delta = \Delta_2$ such that Eq. (3.3-5) reproduces the exact long range interaction energy through $R^{-8}$;

$$\Delta_2 = + \frac{C'_6 + C'_8 R^{-2}}{C_6 + C_8 R^{-2}} \quad (3.3-7)$$

Here $\Delta_2$ is a weak function of $R$.

iii) $\Delta = (\Delta_1, \Delta_3)$. The Unsöld's average energy $\Delta$ is taken to be $\Delta_1$ for the first term and $\Delta_3$ for the second term in Eq. (3.3-4);

$$\bar{E}^{(2)} = -N^2 \left\{ \langle A_{ab}^2 | \psi_4 \rangle | \psi_4 \rangle - \bar{E} \langle A_{ab}^2 | \psi_4 \rangle | \psi_4 \rangle R^{3-4} \Delta_1 \right\}$$

$$+ \left\{ \langle A_{ab}^2 | \psi_4 \rangle | \psi_4 \rangle - \bar{E} \langle A_{ab}^2 | \psi_4 \rangle | \psi_4 \rangle R^{4-1} \Delta_3 \right\} \quad (3.3-8)$$

$\Delta_3$ is chosen such that the second term in Eq. (3.3-5) reproduces the $R^{-8}$ term of the exact long range interaction energy;
\[ \Delta_g = + \frac{C'_8}{C_8} \]  

(3.3-9)

iv) If a point, \( R = R_0 \), on the potential energy curve is known in addition to the lead terms in the exact long range \( R^{-1} \) expansion for interaction energy, another parameter can be introduced. Following Dalgarno and Lynn\textsuperscript{46}, see also Ref. (47), we choose

\[ \Delta = \Delta_i(R_0) = \Delta_i + cS' \quad i = 1 \text{ or } 2 \]  

(3.3-10)

where \( S' \) is the overlap integral given by Eq. (3.3-2) which is a function of \( R \). The parameter \( c \) is determined by reproducing the potential energy curve at the point \( R = R_0 \). In this work this choice of \( \Delta \) is only employed for the \( \text{X}^1\Sigma_g^+ \) state. Here we choose \( R_0 = R_e = 1.401 \ a_0 \), the equilibrium internuclear separation\textsuperscript{90a}.

**Case II:** The \( \text{a}^3\Sigma_g^+ \), \( \text{C}^1\pi_u \), \( 3\pi_g \), \( 1\pi_g \) and \( 3\pi_u \) states of \( \text{H}_2 \).

For these states, when charge overlap and exchange effects are neglected, Eq. (3.3-4) can be written in the form,
\[
\lim_{R \to \infty} \mathcal{E}^{(2)} = -\frac{1}{\Delta} \left\{ \frac{C_6'}{R^6} + \frac{C_8'}{R^8} + \frac{C_{10}'}{R^{10}} + \ldots \right\}. \quad (3.3-11)
\]

Here \( C_6' / \Delta = \tilde{C}_6^{(2)} \) is the "exact" Unsöld's expansion coefficient. \( C_6' / \Delta, C_{10}' / \Delta \) and the coefficients of the higher order terms in \( R^{-1} \) represent only part of the corresponding Unsöld's expansion coefficients. The Unsöld's average energy, \( \Delta \), is chosen as in method (i) for Case I for all these states. Also for the \( C^1 \pi_u \) state, \( \Delta \) is chosen as in method (iv) with \( i = 1 \) for Case I where 90a

\[ R_0 = R_\infty = 1.95219 \ a_0. \]

All other choices of \( \Delta \) discussed in Case I are not applicable here since these choices require the multipole expanded results of Eq. (3.3-4) to reproduce the "exact" Unsöld's expansion of \( E^{(2)} \) through \( O(R^{-8}) \). In order to do this for the states of \( H_2 \) considered here, one has 36 to include the \( V_5 R^{-5} \) term of the multipole expansion of \( V \) in Eq. (3.3-3) for \( \bar{V} \).

The interaction energies through second order, \( \tilde{E}_{ab} \) defined by Eq. (3.2-8), are reported in Tables (3.4-1)-(3.4-7) for the \( X^1 \Sigma_g^+, b^3 \Sigma_u^+, a^3 \Sigma_g^+, C^1 \pi_u, 3 \pi_g, 1 \pi_g \) and \( 3 \pi_u \) states respectively. The second order energies, \( \tilde{E}^{(2)} \), for these states are calculated by using the Unsöld's average
energies discussed in Cases I and II above. Interaction energies calculated by neglecting electron exchange effects are defined as the Coulomb\textsuperscript{5,6,47} energy, $\mathcal{E}_{\text{ab}}^{\text{coul}}$. The Unsöld's average energies, $\Delta$, for the second order Coulomb energies are chosen according to method (iii) for states in Case I and method (i) of Case I for states in Case II. These values of $\mathcal{E}_{\text{ab}}^{\text{coul}}$ are also reported in Tables (3.4-1)-(3.4-7) for all states. The available "exact" interaction energies, $E_{\text{ab}}^{(\text{exact})}$, and the long range interaction energies, $E_{\text{ab}}^{L.R.}$, through $O(R^{-8})$, are also given in the tables for comparison.

All integrals occurring in Eq. (3.3-4) are easily written in terms of standard overlap, nuclear attraction, coulomb and exchange integrals\textsuperscript{101,102} over Slater type atomic orbitals. These integrals are evaluated by using the computer program, "MINTL", written by Janiszewski and Wahl\textsuperscript{102}.

3.4 \textbf{RESULTS AND DISCUSSION}

The results for the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$ and $C^1\Pi_u$ states are given in Tables (3.4-1)-(3.4-4) respectively. Comparing the results for different choices of the Unsöld's average energy, $\Delta$, with the corresponding exact results\textsuperscript{90} one finds that the different choices considered here for $\Delta$ do not
Table 3.4-1 A comparison of some total and Coulomb modified Unsöld's interaction energies through second order with the exact \(^{90a}\) total and long range \(^{56}\) interaction energies for the \(X^1\Sigma^+_g\) state of \(H_2\) as a function of \(R\). The long range results are through \(O(R^{-8})\) only.

<table>
<thead>
<tr>
<th>Energy</th>
<th>(\Delta) used</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_1)</td>
<td>0.1604(0)</td>
<td>0.1358(-1)</td>
<td>0.7259(-3)</td>
<td>0.5113(-4)</td>
<td>0.853(-5)</td>
<td>0.253(-5)</td>
<td>0.962(-6)</td>
<td>0.421(-6)</td>
<td></td>
</tr>
<tr>
<td>(\Delta_2)</td>
<td>0.1532(0)</td>
<td>0.1338(-1)</td>
<td>0.7135(-3)</td>
<td>0.4982(-4)</td>
<td>0.831(-5)</td>
<td>0.248(-5)</td>
<td>0.947(-6)</td>
<td>0.416(-6)</td>
<td></td>
</tr>
<tr>
<td>(-\tilde{E}_{ab})</td>
<td>(\Delta_1(Re))</td>
<td>0.1347(0)</td>
<td>0.1340(-1)</td>
<td>0.7248(-3)</td>
<td>0.5112(-4)</td>
<td>0.853(-5)</td>
<td>0.253(-5)</td>
<td>0.962(-6)</td>
<td>0.421(-6)</td>
</tr>
<tr>
<td>(-\tilde{E}_{ab})</td>
<td>(\Delta_2(Re))</td>
<td>0.1339(0)</td>
<td>0.1324(-1)</td>
<td>0.7126(-3)</td>
<td>0.4982(-4)</td>
<td>0.831(-5)</td>
<td>0.248(-5)</td>
<td>0.947(-6)</td>
<td>0.416(-6)</td>
</tr>
<tr>
<td>((\Delta_1,\Delta_3))</td>
<td>0.1550(0)</td>
<td>0.1340(-1)</td>
<td>0.7136(-3)</td>
<td>0.4979(-4)</td>
<td>0.831(-5)</td>
<td>0.247(-5)</td>
<td>0.947(-6)</td>
<td>0.416(-6)</td>
<td></td>
</tr>
<tr>
<td>(-\tilde{E}_{ab})</td>
<td>((\Delta_1,\Delta_3))</td>
<td>0.2034(-1)</td>
<td>0.1720(-1)</td>
<td>0.1908(-3)</td>
<td>0.3183(-4)</td>
<td>0.7736(-5)</td>
<td>0.2466(-5)</td>
<td>0.9473(-6)</td>
<td>0.4163(-6)</td>
</tr>
<tr>
<td>(-E^{L,R.}_{ab})</td>
<td>0.5875(0)</td>
<td>0.3485(-2)</td>
<td>0.2134(-3)</td>
<td>0.3221(-4)</td>
<td>0.7743(-5)</td>
<td>0.2466(-5)</td>
<td>0.9474(-6)</td>
<td>0.4163(-6)</td>
<td></td>
</tr>
<tr>
<td>(-E_{ab}(exact))</td>
<td>0.1381(0)</td>
<td>0.1637(-1)</td>
<td>0.8150(-3)</td>
<td>0.528(-4)</td>
<td>0.91(-5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>


Table (3.4-2)  A comparison of some total modified Unsöld's interaction energies through second order with the exact\textsuperscript{90a} total interaction energy for the $b^3\Sigma_u^+$ state of H\textsubscript{2} as a function of $R$. See Table (3.4-1) for $\tilde{E}_{\text{coul}}^{ab}$ and $E_{\text{L.R.}}^{ab}$.

<table>
<thead>
<tr>
<th>Energy</th>
<th>$\Delta R$ used</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_1$</td>
<td></td>
<td>-0.1010(0)</td>
<td>-0.7152(-2)</td>
<td>-0.2055(-3)</td>
<td>0.1867(-4)</td>
<td>0.755(-5)</td>
<td>0.253(-5)</td>
<td>0.962(-6)</td>
<td>0.421(-6)</td>
</tr>
<tr>
<td>$\tilde{E}_{\text{coul}}^{ab}$ $\Delta_2$</td>
<td></td>
<td>-0.1077(0)</td>
<td>-0.7295(-2)</td>
<td>-0.2162(-3)</td>
<td>0.1741(-4)</td>
<td>0.733(-5)</td>
<td>0.248(-5)</td>
<td>0.947(-6)</td>
<td>0.416(-6)</td>
</tr>
<tr>
<td>$(\Delta_1, \Delta_3)$</td>
<td></td>
<td>-0.1047(0)</td>
<td>-0.7238(-2)</td>
<td>-0.2142(-3)</td>
<td>0.1747(-4)</td>
<td>0.734(-5)</td>
<td>0.247(-5)</td>
<td>0.990(-6)</td>
<td>0.442(-6)</td>
</tr>
<tr>
<td>$-E_{\text{exact}}^{(ab)}$</td>
<td></td>
<td>-0.1029(0)</td>
<td>-0.6622(-2)</td>
<td>-0.1875(-3)</td>
<td>0.196(-4)</td>
<td>0.67(-5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table (3.4-3) A comparison of some total and Coulomb modified Unsold's interaction energies through second order with the exact total and long range interaction energies for the $a^3\Sigma^+$ state of H$_2$ as a function of R. The long range results are through $O(R^{-8})$ only.

<table>
<thead>
<tr>
<th>Energy</th>
<th>R</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-E^*_{ab}$</td>
<td></td>
<td>0.8145(-1)</td>
<td>0.1383(-1)</td>
<td>0.2962(-2)</td>
<td>0.1512(-2)</td>
<td>0.8283(-3)</td>
<td>0.5324(-3)</td>
<td>0.3824(-3)</td>
<td>0.2841(-3)</td>
</tr>
<tr>
<td>$-E_{coul}^{ab}$</td>
<td></td>
<td>-1.8416(0)</td>
<td>-0.1988(-1)</td>
<td>0.9746(-2)</td>
<td>0.4618(-2)</td>
<td>0.1887(-2)</td>
<td>0.8642(-3)</td>
<td>0.4748(-3)</td>
<td>0.2974(-3)</td>
</tr>
<tr>
<td>$-E_{L.R.}^{ab}$</td>
<td></td>
<td>105.90(0)</td>
<td>0.4624(0)</td>
<td>0.2458(-1)</td>
<td>0.4404(-2)</td>
<td>0.1548(-2)</td>
<td>0.7620(-3)</td>
<td>0.4455(-3)</td>
<td>0.2875(-3)</td>
</tr>
<tr>
<td>$-E_{ab}^{(exact)}$</td>
<td></td>
<td>0.1111(0)</td>
<td>0.3656(-1)</td>
<td>0.5232(-2)</td>
<td>0.1354(-2)</td>
<td>0.7510(-3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table (3.4-4) A comparison of some total and Coulomb modified Unsöld's interaction energies through second order with the exact $^{90a}$ total, and long range $^{36,56}$ interaction energies for the $C_{2v}^{1}$ state of $H_2$ as a function of $R$. The long range results are through $O(R^{-8})$. The total variational interaction energies, $E_{ab}^{(variation)}$, calculated by Browne $^{91a}$ are also given for comparison.

<table>
<thead>
<tr>
<th>Energy</th>
<th>$\Delta_1$</th>
<th>$\Delta_1(R)$</th>
<th>$\Delta_{coul}$</th>
<th>$\Delta_{L,R}$</th>
<th>$E_{ab}^{(exact)}$</th>
<th>$E_{ab}^{(variation)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{ab}$</td>
<td>-0.1343(0)</td>
<td>-0.2853(-1)</td>
<td>-0.2442(-2)</td>
<td>0.4345(-3)</td>
<td>0.4459(-3)</td>
<td>0.2920(-3)</td>
</tr>
<tr>
<td>$\bar{E}_{ab}$</td>
<td>-0.9353(-1)</td>
<td>-0.6011(-1)</td>
<td>-0.2374(-2)</td>
<td>0.4367(-3)</td>
<td>0.4460(-3)</td>
<td>0.2920(-3)</td>
</tr>
<tr>
<td>$E_{ab}^{coul}$</td>
<td>-0.1465(-1)</td>
<td>-0.1273(-3)</td>
<td>0.1121(-2)</td>
<td>0.7729(-3)</td>
<td>0.4698(-3)</td>
<td>0.2927(-3)</td>
</tr>
<tr>
<td>$E_{ab}^{L,R}$</td>
<td>-0.7748(+1)</td>
<td>-0.3916(-1)</td>
<td>-0.4220(-3)</td>
<td>0.6268(-3)</td>
<td>0.4442(-3)</td>
<td>0.2857(-3)</td>
</tr>
<tr>
<td>$E_{ab}^{(exact)}$</td>
<td>-0.9322(-1)</td>
<td>-0.3161(-1)</td>
<td>-0.3342(-2)</td>
<td>0.3585(-3)</td>
<td>0.434(-3)</td>
<td>-</td>
</tr>
<tr>
<td>$E_{ab}^{(variation)}$</td>
<td>-0.8918(-1)</td>
<td>-0.2707(-1)</td>
<td>-0.1892(-2)</td>
<td>0.6598(-3)</td>
<td>0.5188(-3)</td>
<td>0.3176(-3)</td>
</tr>
</tbody>
</table>
yield substantially different results\†. This agrees with the conclusion of Kreek\textsuperscript{47} who used the Brillouin-Wigner perturbation theory in the Unsöld's approximation without modification to calculate the interaction energies for the H(1s)–H\textsuperscript{+}, H(1s)–H(1s) and He(1S)–He(1S) interactions. In general, as expected, better approximate results are obtained for "large" \( R \) and one can safely predict that the modified Unsöld's results represent the exact interaction energies very well for \( R \geq 12 \ a_0 \). Comparing the modified Unsöld's results and the long range results\§ with the exact interaction energies, one can see that the modified Unsöld's results represent the exact interaction energies much better than the long range results for most values of \( R \) quoted in the tables. As expected this is especially true for the excited states where the charge overlap effects persist for very large values of \( R \), see Sec. 2.3 and Ref. (55).

\† The results obtained by using method (iv) in Case I of Sec. 3.3 for \( \Delta \) are substantially better than the other results only for \( R \) near the equilibrium internuclear separation \( R_e = R_0 \)!

\§ For the purpose of this comparison the exact long range results are summed only through \( O(R^{-8}) \) since at most our modified Unsöld's results are strictly valid only through this order in \( R^{-1} \).
In Table (3.4-4) the modified Unsöld's results and the accurate results of Kolos and Wolniewicz\textsuperscript{90a} are compared with the variational potential energy curve of Browne\textsuperscript{91a} for the C$^1\pi_u$ state of H$_2$. It is clear from this comparison that the modified Unsöld's results give a much better representation of the interaction energy than the results obtained by Browne for this state for $R \geq 4$ a$_0$. The modified Unsöld's interaction energies for the $^3\pi_g$, $^1\pi_g$, and $^3\pi_u$ states of H$_2$ are reported in Tables (3.4-5)-(3.4-7) where they are compared with the corresponding ab initio variational energies of Browne\textsuperscript{91}. The modified Unsöld's results are lower in energy than the variational results for $R \geq 8$ a$_0$ and probably furnish reasonably accurate representations of the interaction energy for these excited states of the H$_2$ molecule for these values of the internuclear separation.

Tables (3.4-1)-(3.4-7) contain comparisons of the modified Unsöld's total and coulomb energies for all the states of the H$_2$ molecule discussed above. This data is useful in estimating where exchange and charge overlap effects become important as a function of R, see also Sec. 2.3.

In summary: (i) The modified Unsöld's approximation method discussed in Secs. 3.1C and 3.2 appears to be a
Table (3.4-5) A comparison of the total modified Unsöld's interaction energy through second order with Browne's total variational interaction energy for the $^3\pi_g$ state of H$_2$ as a function of R. See Table (3.4-4) for $\tilde{e}_{ab}^{\text{coul}}$ and $E_{ab}^{L.R.}$.

<table>
<thead>
<tr>
<th>R</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{e}_{ab}$</td>
<td>0.6356(0)</td>
<td>0.3266(-1)</td>
<td>0.4778(-2)</td>
<td>0.1113(-2)</td>
<td>0.4936(-3)</td>
<td>0.2935(-3)</td>
<td>0.1910(-3)</td>
<td>0.1306(-3)</td>
</tr>
<tr>
<td>$E^{(\text{variation})}_{ab}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1339(-2)</td>
<td>0.564(-3)</td>
<td>0.319(-3)</td>
<td>-</td>
<td>0.135(-3)</td>
</tr>
</tbody>
</table>
Table (3.4-6) A comparison of the total and Coulomb modified Unsöld's interaction energies through second order with Browne's total variational $^{91b}$ and long range $^{36,56}$ interaction energies for the $^1\Pi_g$ state of $H_2$ as a function of $R$. The long range results are through $O(R^{-8})$ only.

<table>
<thead>
<tr>
<th>Energy</th>
<th>R</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma_{ab}$</td>
<td></td>
<td>-0.5725(0)</td>
<td>-0.2541(-1)</td>
<td>-0.1357(-2)</td>
<td>0.7667(-3)</td>
<td>0.5676(-3)</td>
<td>0.3402(-3)</td>
<td>0.2117(-3)</td>
<td>0.1399(-3)</td>
</tr>
<tr>
<td>$\Sigma_{coulab}$</td>
<td></td>
<td>0.7943(-2)</td>
<td>0.9146(-2)</td>
<td>0.3210(-2)</td>
<td>0.1298(-2)</td>
<td>0.6250(-3)</td>
<td>0.3463(-3)</td>
<td>0.2124(-3)</td>
<td>0.1400(-3)</td>
</tr>
<tr>
<td>$\Sigma_{LRab}$</td>
<td></td>
<td>0.5677(0)</td>
<td>0.4787(-1)</td>
<td>0.5223(-2)</td>
<td>0.1507(-2)</td>
<td>0.6600(-3)</td>
<td>0.3552(-3)</td>
<td>0.2155(-3)</td>
<td>0.1414(-3)</td>
</tr>
<tr>
<td>$\Sigma_{E(variation)}$</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.583(-3)</td>
<td>0.509(-3)</td>
<td>0.319(-3)</td>
<td>-</td>
<td>0.136(-3)</td>
</tr>
</tbody>
</table>
Table (3.4-7) A comparison of the total modified Unsöld's interaction energy through second order with Browne's total variational interaction energy for the $^3\pi_u$ state of H$_2$ as a function of R. See Table (3.4-6) for $g_{ab}^{coul}$ and $L.R.$.

<table>
<thead>
<tr>
<th>R</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{E_{ab}}{\text{ Energy}}$</td>
<td>0.4778(-1)</td>
<td>0.3811(-1)</td>
<td>0.7645(-2)</td>
<td>0.1828(-2)</td>
<td>0.6823(-3)</td>
<td>0.3524(-3)</td>
<td>0.2131(-3)</td>
<td>0.1401(-3)</td>
</tr>
<tr>
<td>$-E_{ab}$ (variation)</td>
<td>0.1083(0)</td>
<td>0.4280(-1)</td>
<td>0.8291(-2)</td>
<td>0.1743(-2)</td>
<td>0.6288(-3)</td>
<td>0.3264(-3)</td>
<td>-</td>
<td>0.1360(-3)</td>
</tr>
</tbody>
</table>
simple useful way to avoid the difficulty of evaluating matrix elements of $H^2$ in the calculation of the second order energy via the Brillouin-Wigner perturbation theory. Indeed the results\textsuperscript{47} obtained by using the full Unsöld's treatments (see Sec. 3.1C) and the modified treatments are not markedly different for the ground state of $H_2$ for most values of $R$, see Table (3.4-8). (ii) This approximate method is an effective way to incorporate charge overlap and exchange effects into the long range treatment of intermolecular forces for large $R$ where accurate variational results are usually not available. The modified Unsöld's method will be very useful for excited states where charge overlap effects persist for large values of $R$. (iii) The modified Unsöld's method also avoids the difficulty of treating the divergent integrals involving $H^3$ which occurs in the third order energy of the full Unsöld's treatments. (iv) The modified Unsöld's interaction energies for the $^3
u_g$, $^1
u_g$ and $^3
u_u$ states of $H_2$ are probably the most accurate representation of the potential energy curves for these states for $R \geq 8$ $a_0$ that are available at the present time.
Table (3.4-8) A comparison of the total modified Unsöld's interaction energy through second order with Kreek's 47 'exact' Unsöld's interaction energy, \( \mathcal{E}_{ab}^{(Kreek)} \), through second order for the \( \chi^1\Sigma^+ \) state of \( \text{H}_2 \) as a function of \( R \). The exact interaction energies 90a are also given for comparison. The Unsöld's energies are evaluated with the Unsöld average energy \( \Delta_1 \) discussed in Case I of Sec. 3.3.

<table>
<thead>
<tr>
<th>R</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\mathcal{E}_{ab} )</td>
<td>0.16036(0)</td>
<td>0.13579(-1)</td>
<td>0.72594(-3)</td>
<td>0.5113(-4)</td>
<td>0.853(-5)</td>
<td>0.253(-5)</td>
<td>0.962(-6)</td>
</tr>
<tr>
<td>( -\mathcal{E}_{ab}^{(Kreek)} )</td>
<td>0.21538(0)</td>
<td>0.19889(-1)</td>
<td>0.10373(-2)</td>
<td>0.66103(-4)</td>
<td>0.94588(-5)</td>
<td>0.26378(-5)</td>
<td>0.98176(-6)</td>
</tr>
<tr>
<td>( -E_{ab}^{(exact)} )</td>
<td>0.13813(0)</td>
<td>0.16369(-1)</td>
<td>0.8150(-3)</td>
<td>0.528(-4)</td>
<td>0.91(-5)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4. FLOATING ONE AND TWO CENTRE CALCULATIONS OF INTERMEDIATE AND LONG RANGE INTERMOLECULAR FORCES

It has been shown\textsuperscript{23,24} that the fixed one centre method can give accurate results for the energies of diatomic molecules near their equilibrium separation. However this method misbehaves\textsuperscript{27,28} for large values of $R$, see Sec. 4.1. It is also well known\textsuperscript{1,2,10,32} that perturbation theory treatments of the long range intermolecular forces can give excellent results for diatomic molecules at large $R$. The motivation for the floating centre(s) method is to attempt to develop an approach for calculating intermediate range interaction energies for diatomic molecules by extending the fixed one centre method so that it smoothly reproduces the long range approach as $R$ becomes large.

In this Chapter the fixed one centre method is briefly reviewed and discussed in Sec. 4.1. Some modifications of the fixed one centre method for large $R$ are suggested in Sec. 4.2. In Sec. 4.3 the floating centre(s) method is discussed in detail by using the perturbation theory and variational method approaches. In Sec. 4.4 this floating centre(s) approach is used to calculate the interaction
energies for the ground state \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules by the variational method.

4.1 BRIEF REVIEW AND DEFICIENCIES OF THE FIXED ONE CENTRE METHOD

The fixed one centre method has been used to calculate the electronic energies of a number of molecules in their equilibrium configuration or its neighbourhood. The results of these calculations are fairly good although there are convergence problems with the approach (see below). Surveys of one centre calculations have been given in the review articles by Bishop\(^{23}\) and by Hayes and Parr\(^{24}\). The choice of the expansion centre is arbitrary. However in many cases there will be an "intuitively logical" choice, for example the internuclear midpoint for a homonuclear diatomic molecule or the heavy nucleus of a heteronuclear diatomic molecule. It must be emphasized that in the fixed one centre method the expansion centre is not a function of the molecular configuration.

4.1A HOMONUCLEAR DIATOMIC MOLECULES

Let us consider first homonuclear diatomic molecules where the expansion centre is chosen at the internuclear midpoint in the fixed one centre method. While one centre calculations can give good results for these molecules at
their equilibrium separations, there is a serious drawback shown clearly by variational calculations using this method. That is the rate of convergence to the exact results, as the number of configurations in the variational trial wavefunction increases, is very slow; see for example the detailed analysis given by Howell and Shull, Hagstrom and Shull, and Joy and Handler for the ground state $H_2^+$ and $H_2$ molecules, see also Table (4.1-1) below. This problem of slow convergence also appears in one centre perturbation theory calculations; see for example the calculations by Mackrodt.

Some one centre results for the interaction energy of the ground state $H_2^+$ and $H_2$ molecules at their equilibrium separations are given in Table (4.1-1). The efficiency of the one centre method at "small" internuclear separation can be seen by comparing these energies with the corresponding exact values. The slow rate of convergence with respect to the usual two centre calculation is revealed by the large number of configurations and the high order of perturbation theory needed in the one centre calculations to obtain accurate results (see Table (4.1-1)). This convergence problem at "small" internuclear separation has been attributed to the deficiency of the one centre wavefunction in reflecting the singularities of potential
Table (4.1-1) Some fixed one centre results for the interaction energy, $E_{ab}$, of ground state $H_2^+$ and $H_2$ at their equilibrium separations. The expansion centre is at the internuclear midpoint and V and P indicate results obtained by variational and perturbation theory one centre calculations respectively.

<table>
<thead>
<tr>
<th>$H_2^+$</th>
<th>$Re = 2 , a_0 , E_{ab} \text{ (exact)} = -0.10263$</th>
<th>$H_2$</th>
<th>$Re = 1.4 , a_0 , E_{ab} \text{ (exact)} = -0.17447$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{E}_{ab}$</td>
<td>Method</td>
<td># of Conf. or Order of Pert.</td>
<td>Reference</td>
</tr>
<tr>
<td>0.09563</td>
<td>V</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>0.101206</td>
<td>V</td>
<td>14</td>
<td>105</td>
</tr>
<tr>
<td>0.09771</td>
<td>V</td>
<td>5</td>
<td>106</td>
</tr>
<tr>
<td>0.10240</td>
<td>V</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>0.5956</td>
<td>P</td>
<td>2</td>
<td>107</td>
</tr>
<tr>
<td>0.0899</td>
<td>P</td>
<td>2</td>
<td>29</td>
</tr>
<tr>
<td>0.1027</td>
<td>P</td>
<td>5</td>
<td>27</td>
</tr>
</tbody>
</table>
energy at the nuclear positions (the cusp condition) and
to the introduction of a new unphysical singularity at the
expansion centre.

The fact that the rate of convergence of the one centre
method depends on the molecular configuration has been
indicated by several authors25,26,29. Dvůřáček and Horák28
and Mackrodt27 have pointed out the decrease in the rate of
convergence of the method as the internuclear separation
increases, see also Ref. (115). If one considers the
problem at large values of R characteristic of molecular
dissociation, it is clear that the fixed one centre method
must "misbehave" badly at large R. That is the one centre
method can not properly describe the process of dissociation
for homonuclear diatomic molecules since the electron(s) are
not localized around the internuclear midpoint as R increases.‡

The misbehaviour of the fixed one centre method for
large R can be illustrated explicitly by using some one
centre variational results for the energy of the ground
state \( H_2^+ \) and \( H_2 \) molecules, see Secs. 4.3 and 4.4 for details.

‡ This can also be explained by the cusp condition
mentioned above. As the internuclear separation increases,
the cusp conditions at both nuclei are more difficult to
satisfy by a wavefunction centred at the internuclear
midpoint.
Here only the results for $\text{H}_2^+$ and $\text{H}_2$ obtained from the simple STO (Slater type orbital) basis sets $\{1s, 2s\}$ and $\{1s^2, 2p^2\}$ respectively are used. The ratio, $R$, of the interaction energy obtained from these variational calculations to the corresponding exact results$^{90a, 112}$ are given as a function of $R$ in Figs. (4.1-1) and (4.1-2) respectively,

$$R = \frac{\tilde{E}_{ab}}{E_{ab}(\text{exact})}. \quad (4.1-1)$$

One can see from these results that the one centre results diverge very rapidly from the exact results and even give the wrong sign with respect to the exact results for large $R$.

4.1B *HETERONUCLEAR DIATOMIC MOLECULES*

The fixed one centre method has also been used to calculate the energies of heteronuclear diatomic molecules where the expansion centre is chosen at the heavy nucleus. The results behave differently for large values of $R$ depending on the type of the heteronuclear diatomic molecules considered. For heteronuclear diatomic molecules that dissociate to give a "bare" nucleus such as the ground state $\text{HeH}^+$ and $\text{HeH}^+$ molecules$^{27, 115-117}$, there is no misbehaviour at large $R$. This is because the choice of the heavy nucleus as expansion centre is correct when these
Fig. (4.1-1) Comparison of the interaction energy calculated from the fixed internuclear midpoint one centre method using the basis set \{1s, 2s\} with the corresponding exact results for ground state \( \text{H}_2^+ \) as a function of \( R \). \[ R = \frac{E_{ab}}{E_{ab} \text{ (exact)}}. \]
Fig. (4.1-2) Comparison of the interaction energy calculated from the fixed internuclear midpoint one centre method using the basis set \{1s^2, 2p^2\} with the corresponding exact results for ground state \(H_2\) as a function of \(R\). \(R = \frac{\tilde{E}_{ab}}{E_{ab}(\text{exact})}\).
molecules dissociate. However for heteronuclear diatomic molecules which dissociate into two species, both having electrons associated with them, one can anticipate that "misbehaviour" will occur at large $R$. Clearly a single expansion centre at the heavy nucleus can not describe the dissociation properly since the light nucleus also has some electrons associated with it upon dissociation.

4.2 **MODIFICATION OF THE FIXED ONE CENTRE METHOD**

In order to correct the misbehaviour for large $R$ and also to attempt to speed up the convergence in the (fixed) one centre method for all $R$, the expansion centre can be allowed to move freely along the internuclear axis as a function of the internuclear separation. The location of the expansion centre is determined optimally as a function of $R$ (see Sec. 4.4).

4.2A **HOMONUCLEAR DIATOMIC MOLECULES**

The simplest homonuclear diatomic molecule ground state $H_2^+$, which dissociates into a proton and a hydrogen atom, can serve as a good example for this modification of the fixed one centre method. Here the optimized centre will be at the internuclear midpoint for small values of $R$ and can relocate at any place between the midpoint and a proton (or at a proton) as $R$ increases. This idea has been used by Tamassy-Lentei and Babá to investigate the.
importance of the position of the expansion centre in their one centre calculations of \( H_2^+ \). However they have only investigated the energy for several small values of \( R \) (\( \leq 3.6 \ a_0 \)) and therefore were not able to indicate the importance of "floating" the expansion centre for all \( R \), see however Ref. (115).

The benefit of this "floating" centre approach is illustrated here by a very simple variational calculation of the ground state energy of \( H_2^+ \), see Sec. 4.4B for details. Here only the results obtained from the simple STO \( \{1s, 2s\} \) basis set referred to the floating centre are used. The ratio, \( R \), defined by Eq. (4.1-1), is shown as a function of \( R \) in Fig. (4.2-1). Comparing Figs. (4.2-1) with (4.1-1) one can see clearly that the gross misbehaviour of the fixed one centre method at large \( R \) is removed although the results obtained from this floating centre approach are still far from the exact values. It must be noted however, that the results at large \( R \) can be easily improved by incorporating proper long range configurations in the basis set.

Corresponding calculations have also been done for the ground state \( H_2 \) molecule using the simple STO \( \{1s^2, 2p^2\} \) basis set referred to the floating centre. The results for the ratio \( R \) defined by Eq. (4.1-1), as a function of \( R \),
Fig. (4.2-1) Comparison of the interaction energy calculated from the floating one
centre method using the basis set {1s, 2s} with the corresponding exact
results for ground state H$_2^+$ as a function of R. \( \mathcal{R} = \frac{\tilde{E}_{ab}}{E_{ab} \text{(exact)}} \).
is essentially the same as those for the fixed one centre
calculations shown in Fig. (4.1-2) and misbehaviour occurs
at large $R$. This is not difficult to understand since
normal dissociation of a hydrogen molecule will give two
hydrogen atoms and a one centre (fixed or floating) approach
can not describe this dissociation properly. To correct
this procedure one generalizes the method by incorporating
two floating centres into the treatment, see Sec. 4.3 for
details. Each floating centre will be the expansion centre
associated with one electron. For small values of $R$ the
two centres coalesce at the internuclear midpoint and for
large $R$ the centres are allowed to float along the inter-
nuclear axis to the nuclei of the interacting atoms. This
idea is illustrated by a simple variational calculation of
the ground state energy for $H_2$, see Sec. 4.4C for details.
The ratio $R$, obtained by using the simple $\{1s^2,2p^2\}$ basis
set now centred at the two floating expansion centres, is
given as a function of $R$ in Fig. (4.2-2). The importance
of floating two centres is easily seen by comparing Figs.
(4.2-2) with (4.1-2).

4.2B HETERONUCLEAR DIATOMIC MOLECULES

Attempts to improve the convergence of the one centre
method by floating the single expansion centre have been
Fig. (4.2-2) Comparison of the interaction energy calculated from the floating two centre method using the basis set \([1s^2, 2p^2]\) with the corresponding exact results for ground state \(H_2\) as a function of \(R\).

\[ R = \frac{E_{ab}}{E_{ab}^{(exact)}} \]
made by several authors for some heteronuclear diatomic molecules and a few larger molecules containing a heavy atom. Bishop, Hoyland and Parr\textsuperscript{119} and Bishop and Hoyland\textsuperscript{120} have treated the location of the expansion centre as an additional variable in one centre calculations of the energy for the NH\textsubscript{3}, H\textsubscript{2}O, HF molecules and the first row diatomic hydrides. Combs and Runnels\textsuperscript{116} have applied this idea to investigate the HeH\textsuperscript{2+} and HeH\textsuperscript{+} molecules. Tamásey-Lentei\textsuperscript{117} has also investigated HeH\textsuperscript{2+} and HeH\textsuperscript{+} and other similar molecules such as HBe\textsuperscript{4+} and HeBe\textsuperscript{5+}. The improvement in energy obtained by optimizing the position of the expansion centre is minimal for all molecules of this type where the expansion centre stays very close to the nucleus of the heavy atom, see also Ref. (115).

4.3 **THE FLOATING CENTRE(S) METHOD**

The floating centre(s) method introduced in Sec. 4.2 is discussed formally using a perturbation theory approach. The relation between the theory of long range interaction energies including charge overlap effects, see Sec. 2.1, and the floating centre(s) method as well as the relation between the fixed one centre method and the floating centre(s) method are discussed in detail. The variational method approach to the floating centre(s) method is also
outlined for use in the test calculations discussed in Sec. 4.4.

4.3A PERTURBATION THEORY APPROACH

Consider a diatomic molecule consisting of nucleus "a", with charge $Z_a$, and nucleus "b", with charge $Z_b$, and N electrons \{p\} or \{q\}. The non-relativistic Hamiltonian for this system is given by

$$H = \sum_{p=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_p^2 - \frac{Z_a}{r_{ap}} - \frac{Z_b}{r_{bp}} + \sum_{q>p}^{N} \frac{1}{r_{pq}} \right\} + \frac{Z_a Z_b}{R} \quad (4.3-1)$$

If the internuclear distance, $R$, becomes large, this diatomic molecule dissociates to form two species, atom "a" containing the nucleus a and $N_a$ electrons \{i\} or \{k\} and atom "b" containing the nucleus b and $N_b$ electrons \{j\} or \{l\}. When $R = \infty$ the isolated atoms "a" and "b" correspond to the zeroth order problem in the perturbation theory treatments of intermolecular forces discussed in Sec. 2.1. For finite $R$, if the electron exchange effects are neglected, a perturbation solution for the Schrödinger equation of this system can be developed in the way discussed in Sec. 2.1. Here the zeroth order Hamiltonian $H_0$ and the interaction potential energy $V$ defined by Eqs. (2.1-2) and (2.1-3) will be
\[ H_o = H_o(a) + H_o(b) \]  \hspace{1cm} (4.3-2)

where

\[ H_o(a) = \sum_{i}^{N_a} \left\{ -\frac{1}{2} \nabla_i^2 - \frac{Z_a}{r_{ai}} + \frac{1}{\sum_{k \neq i}^{N_b} r_{ki}} \right\} \]  \hspace{1cm} (4.3-3)

\[ H_o(b) = \sum_{j}^{N_b} \left\{ -\frac{1}{2} \nabla_j^2 - \frac{Z_b}{r_{bj}} + \frac{1}{\sum_{i \neq j}^{N_b} r_{lj}} \right\} \]  \hspace{1cm} (4.3-4)

and

\[ \mathcal{V} = H - H_o \]  \hspace{1cm} (4.3-5)

The perturbation theory approach discussed in Sec. 2.1 has been shown\textsuperscript{2,5,10,32} to be very effective in calculating the long range intermolecular forces where the charge overlap effects are also neglected. However the long range results for the interaction energy thus obtained are known to be a asymptotically divergent series in powers of \( R^{-1} \) for all finite values of \( R \) and this asymptotic nature is readily apparent as \( R \) decreases; see Chapter 2. The asymptotic nature can be corrected by incorporating the charge overlap effects, see Secs. 2.3, 2.4 and Ref. (5), but this perturbation theory is well known\textsuperscript{2,5,10,32} not to be suitable for use at small \( R \) where the electron exchange effects are appreciable.
It has been pointed out in Sec. 4.1 that the fixed one centre method can provide exchange effects in the calculation of the energy for diatomic molecules at small \( R \). This suggests that one can incorporate the exchange effects into the perturbation theory approach using wavefunctions which are not antisymmetrized with respect to the exchange of electrons between "a" and "b" by a simple modification of the perturbation theory outlined in Sec. 2.1. That is one introduces two phantom centres (imaginary nuclei), "c" which is a distance \( \rho_a \) from nucleus "a" and "d" which is a distance \( \rho_b \) from nucleus "b", along the internuclear axis between "a" and "b"; see Fig. (4.3-1).

In this case one can write the Hamiltonian \( \hat{H} \) in a form similar to that given by Eqs. (4.3-1) - (4.3-5):

\[
\hat{H} = \hat{H}_o + \hat{V}
\]

\[
\hat{H}_o = \hat{H}_o(c) + \hat{H}_o(d)
\]

\[
\hat{H}_o(c) = \sum_{i}^{N_a} \left\{ -\frac{1}{2} \nabla_i^2 - \frac{Z_c}{\gamma_{ci}} + \sum_{k>i}^{N_a} \frac{1}{\gamma_{ki}} \right\}
\]

\[
\hat{H}_o(d) = \sum_{j}^{N_b} \left\{ -\frac{1}{2} \nabla_j^2 - \frac{Z_d}{\gamma_{dj}} + \sum_{l>j}^{N_b} \frac{1}{\gamma_{lj}} \right\}
\]
Fig. (4.3-1) Coordinate systems for the floating centre(s) method

(a) Two centres
(b) One centre
\[ \hat{V} = \hat{H} - \hat{H}_0 \]  \hspace{1cm} (4.3-10)

Here if one considers \( \hat{H}_0 \) and \( \hat{V} \) as the zeroth order Hamiltonian and the interaction potential energy respectively, a perturbation solution to the Schrödinger equation can be developed in the way discussed in Sec. 2.1. The results for the wavefunction and energy of the diatomic molecule are analogous to those given in Sec. 2.1. For example one obtains results similar to Eqs. (2.1-6)-(2.1-12) by replacing in these equations \( \hat{H}_0, \hat{V}, \hat{\Psi}^{(n)} \) and \( \hat{E}^{(n)} \) by \( \hat{H}_0, \hat{V}, \hat{\Psi}^{(n)} \) and \( \hat{E}^{(n)} \) respectively. The interaction energy, \( E_{ab} \), through \( n \)-th order is given by

\[ E_{ab} = \hat{E}^{(0)} + \hat{E}^{(1)} + \hat{E}^{(2)} + \cdots + \hat{E}^{(n)} - E^{(0)} \]  \hspace{1cm} (4.3-11)

where \( E^{(0)} \) is the energy of the two isolated atoms. If the interaction energy is optimized with respect to \( \rho_a \) and \( \rho_b \), it is clear that as \( R \to \infty \), \( \rho_a \to 0 \) and \( c \to a, d \to b \). Thus for large \( R \) one recovers Eqs. (4.3-2)-(4.3-5) from Eqs. (4.3-7)-(4.3-10) and this treatment yields the method discussed in Sec. 2.1A. Therefore the interaction energy is given by Eq. (2.1-18) since \( \hat{E}^{(n)} \to E^{(n)} \) for large \( R \).
If one treats $\rho_a$ and $\rho_b$ as variables, the advantages of using floating phantom centres to attempt to recover exchange effects can be shown by considering different choices of $\rho_a$ and $\rho_b$; see also Ref. (115) for the one electron case.

**Homonuclear Diatomic Molecule** $(Z_a = Z_b)$

I) Set $\rho_a = \rho_b = R/2$ and $c = d$. This treatment corresponds to the fixed one centre method for homonuclear diatomic molecules where the expansion centre is chosen at the internuclear midpoint. This fixed one centre treatment can give accurate results for the interaction energy for small $R$; see Table (4.1-1). As $R$ increases the results from this treatment converge very slowly to the exact results and, as illustrated in Sec. 4.1, are very poor at long range. It has been shown in Sec. 4.2 that in order to obtain reasonable results for large $R$ the expansion centre should have the freedom to shift to one of the nuclei or to "split" into two floating centres; see Cases III and IV below.

II) Set $\rho_a = \rho_b = 0$, $c = a$, $d = b$. In this case $H_0 = H_0$, $V = V$ and this treatment corresponds to the perturbation method considered in Sec. 2.1 for a diatomic system. It can give reasonable results that include charge
overlap effects for large R and exact \( R^{-1} \) long range results.

III) Set \( \rho_a = \rho_b = \rho \) and determine \( \rho \) variationally (see next section) as a function of R. This yields the "floating two centre" treatment. This method can give accurate results for small R since one can show \( \rho \to R/2 \) as \( R \to 0 \) corresponding to Case I. It can also give reasonable results for large R and exact long range \( R^{-1} \) results because \( \rho \to 0, c \to a, d \to b \) as \( R \to \infty \) and one recovers Case II.

IV) Set \( \rho_a = \rho, \rho_b = R-\rho, c = d \) and determine \( \rho \) variationally as a function of R. This gives the "floating one centre" treatment. It is a special limit of Case III when "atom" a or b is a bare nucleus. This treatment can give accurate results for the interaction energy at small R since it can be shown \( \rho \to R/2 \) as \( R \to 0 \). However it can only give reasonable results for large R and exact long range \( R^{-1} \) results for molecules which dissociate to give a "bare" nucleus; see for example the discussion in Sec. 4.2.

Heteronuclear Diatomic Molecules \( (Z_a > Z_b) \)

I) Set \( \rho_a = \rho_b = R/2, c = d \). This yields the fixed one centre treatment with the expansion centre at the
internuclear midpoint. It gives reasonable results only for very small $R$ and poor results for large $R$; see for example Refs. (29,115) for calculations on the $\text{HeH}^{2+}$ molecule. It is also clear that the expansion centre should have freedom to float or "split" into two floating centres in order to obtain reasonable results for large $R$.

II) Set $\rho_a = 0$, $\rho_b = R$, $c = d = a$. This corresponds to the fixed one centre treatment with the expansion centre at the heavy nucleus. This treatment can give accurate results for small $R$; see for example Refs. (27, 29, 115) for calculations on the ground state $\text{HeH}^{2+}$ molecule. However it only gives good long range results for molecules which dissociate to give the "bare" nucleus of the light atom.

It should be pointed out that in Cases I and II a more appropriate choice of the expansion centre for small $R$ is the charge centre, $\rho_a = \frac{Z_b R}{Z_a + Z_b}$, $\rho_b = \frac{Z_a R}{Z_a + Z_b}$; see for example Refs. (115,121).

III) Set $\rho_a = \rho_b = 0$, $c = a$, $d = b$. This yields the perturbation treatment considered in Sec. 2.1 for a diatomic system. The results are similar to Case II for homonuclear molecules.
IV) Determine $\rho_a$ and $\rho_b$ variationally as functions of $R$.
This corresponds to the floating two centre treatment for heteronuclear diatomic molecules. This treatment can give accurate results for small and large $R$ since
\[ \rho_a \rightarrow \frac{Z_b}{Z_a + Z_b}, \quad \rho_b \rightarrow \frac{Z_a}{Z_a + Z_b} \]
as $R \rightarrow 0$ and $\rho_a = \rho_b \rightarrow 0$ as $R \rightarrow \infty$ (see Case III).

V) Set $\rho_a = \rho$, $\rho_b = R - \rho$ and determine $\rho$ variationally as a function of $R$. This gives the floating one centre treatment. It is also a special case of the floating two centre treatment when the light "atom" is a bare nucleus. This treatment clearly can give accurate results for small $R$ since
\[ \rho \rightarrow \frac{Z_b}{Z_a + Z_b} \]
as $R \rightarrow 0$ to give the charge centre calculation. However it can only give accurate long range results for molecules which dissociate to give the "bare" nucleus of the light atom since $\rho \rightarrow 0$ as $R \rightarrow \infty$. It must be noted that this treatment yields nearly the same results obtained from Case II since the expansion centre stays very close to the nucleus of the heavy atom 115-117.

It should be emphasized that in general for homonuclear and heteronuclear molecules which dissociate into two species both having electrons associated with them the floating two centre treatment should be used in order to obtain reasonable results for all $R$. 
4.3B VARIATIONAL METHOD APPROACH

The Schrödinger equation, Eq. (2.1-1), can be solved via the variational method in which the expectation value of the Hamiltonian, \( \tilde{\mathcal{E}} \), is an upper bound to the ground state energy \( E_0 \) of the system under consideration;

\[
E_0 \leq \tilde{\mathcal{E}} = \frac{\langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad \text{(4.3-16)}
\]

Here \( \mathcal{H} \) is the Hamiltonian for the system and \( \tilde{\Psi} \) the trial wavefunction.

For the diatomic system considered in Sec. 4.3A, the Hamiltonian \( \mathcal{H} \) is given by Eq. (4.3-1). The trial wavefunction \( \tilde{\Psi} \), in the floating centre(s) treatment discussed in Sec. 4.3A, can be taken to be a linear combination of the product functions, \( \varphi_c(u) \varphi_d(u') \),

\[
\tilde{\Psi} = \sum_u \sum_{u'} C_{uu'} \varphi_c(u) \varphi_d(u') \equiv \sum_k C_k \Psi_k \quad \text{(4.3-17)}
\]

where \( \varphi_c(u) \) and \( \varphi_d(u') \) are arbitrary many electron wavefunctions for the \( N_a \) electrons referred to the centre \( c \) and the \( N_b \) electrons referred to the centre \( d \) respectively. The coefficients \( C_k \) and the value of \( \tilde{\mathcal{E}} \) are obtained by solving the secular equations:

\[
\sum_k C_k (\mathcal{H}_{\ell_k} - \tilde{\mathcal{E}} S_{\ell_k}) = 0 \quad ; \quad k, \ell = 1, 2, 3, \ldots \quad \text{(4.3-18)}
\]
where
\[ H_{\ell k} = \langle \Psi_{\ell} | H | \Psi_{k} \rangle \]  (4.3-19)
\[ S_{\ell k} = \langle \Psi_{\ell} | \Psi_{k} \rangle \]  (4.3-20)

The minimum value of \( \bar{E} \) for a particular choice of the trial wavefunction \( \bar{\Psi} \) is found by varying systematically the screening constants in the \( \varphi \)'s and the position(s) of the floating centre(s) as variational parameters. The variational procedures are discussed further in Appendix F.

4.4 VARIATIONAL FLOATING CENTRE(S) CALCULATIONS FOR \( H_2^+ \) and \( H_2 \)

The ground state \( H_2^+ \) and \( H_2 \) molecules are used as model systems for testing the feasibility of using the floating centre(s) method to calculate the interaction energy for all \( R \). The treatments for these molecules can be easily generalized to heteronuclear diatomic molecules and diatomic molecules with more than two electrons. The ground states of these molecules are considered since in the fixed one centre calculations for them the convergence with respect to the exact results as a function of the number of configurations used in the trial wavefunction is extremely slow for \( R \) greater than the equilibrium internuclear
separation. (The convergence for the excited states \(23,91b, 117,122\) and for heteronuclear diatomic molecules is much faster; see Secs. 4.1 and 4.5). Thus if the floating one centre calculations yield satisfactory results for the interaction energy for these test molecules the method can be expected to work well for more favourable cases.

The variational method is used for the calculations since it has been used for most of the fixed one centre calculations in the literature \(23,24\). The variational method is also very useful since it gives an upper bound to the exact total energy. Thus for example, the method yields a convenient way\(^*\) for obtaining the optimum value of the floating parameters \(\rho_a\) and \(\rho_b\) (see below). The interaction energy, \(\tilde{E}_{ab}\), is obtained from

\[
\tilde{E}_{ab} = \tilde{E} - E^{(0)} \tag{4.4-1}
\]

where \(\tilde{E}\) is defined by Eq. (4.3-16) and \(E^{(0)}\) is the energy of the isolated atom(s).

\* In the perturbation theory calculations of the floating centre(s) methods, there are many ways to obtain the optimum value of the variational parameters, see Refs. (18, 29, 115).
4.4A METHOD OF CALCULATION

The one electron basis set used to form the trial wavefunctions for the $H_2^+$ and the $H_2$ molecules are normalized Slater type orbitals (STO's) given by\textsuperscript{102b,123}

$$\chi_{n,\ell}^{m}(\alpha_i) = (2\eta)^{n+\frac{1}{2}} \left[ (2n)! \right]^{-\frac{1}{2}} \gamma^{n-1} \exp(-\gamma \rho) \chi_{\ell}(\rho, \varphi).$$

(4.4-2)

Here $n$, $\ell$ and $m$ are the principal, azimuthal and magnetic quantum numbers respectively, $\eta$ is a screening constant and $(\alpha_i)$ indicates that the one electron wavefunction is for electron $i$ referred to centre $\alpha$.

For the one electron diatomic molecule $H_2^+$ in the $^2\Sigma^+$ state, the trial wavefunction $\widetilde{\psi}$ has the form

$$\widetilde{\psi} = \sum_{n=1}^{\infty} \sum_{\ell=0}^{\infty} C(n, \ell) \chi_{n,\ell}^{c}$$

(4.4-3)

where $\chi(c)$ represents an STO referred to centre "c", see Fig. (4.3-1), and the superscript $m$ on $\chi$ is neglected since it is zero for $\Sigma$ states. The Hamiltonian $H$ for this molecule can be easily obtained from Eq. (4.3-1) by setting $N = 1$ and $Z_a = Z_b = 1$. It must be noted here that a "$1s$" STO must be included in Eq. (4.4-3) when one considers the ground state of $H_2^+$ in order to represent the dissociation to form a "$1s$" hydrogen atom and a proton as $R \to \infty$. 
For the two electron diatomic molecule $H_2$ in the $^1\Sigma_g^+$ ground state, the trial wave function $\widetilde{\Psi}$ is given by

$$\widetilde{\Psi} = \sum_{n=1}^{\infty} \sum_{\ell=0}^{n} \sum_{n'=1}^{\infty} \sum_{\ell'=0}^{n'} \sum_{m=0}^{1} C(n, \ell, n', \ell', m) [ (n, \ell, m)(n', \ell', -m)] (4.4-4)$$

$$[(n, \ell, m)(n, \ell, -m)] = N' \left[ \chi_{n, \ell}^{(m)} \chi_{n', \ell'}^{(-m)} + \chi_{n, \ell'}^{(-m)} \chi_{n', \ell}^{(m)} \right], \quad (4.4-5)$$

$$[(n, \ell, m)(n', \ell', -m)] = N' \left[ \chi_{n', \ell'}^{(m)} \chi_{n, \ell}^{(-m)} + \chi_{n', \ell}^{(-m)} \chi_{n, \ell'}^{(m)} + \delta \chi_{n, \ell}^{(m)} \chi_{n', \ell'}^{(-m)} + \delta \chi_{n', \ell'}^{(-m)} \chi_{n, \ell}^{(m)} \right], \quad (n, \ell', \ell' \neq (n', \ell')) (4.4-6)$$

where $N'$ is a normalization constant, and $\chi (c1)$ and $\chi (d2)$ represent STO's for electrons 1 and 2 referred to the centres "c" and "d" respectively; see Fig. (4.3-1). Here $m' = -m$ since $(m+m')$ must be zero for $\Sigma$ states, $\delta = +1$ if $(-1)^{\ell+\ell'} = 1$ and $\delta = -1$ if $(-1)^{\ell+\ell'} = -1$ for $g$ states (right handed coordinate systems are used in this thesis, see Fig. (2.2-1)). The Hamiltonian for the $H_2$ molecule is obtained from Eq. (4.3-1) by setting $N = 2$ and $Z_a = Z_b = 1$. Also for ground state $H_2$ the product function $1s(c1)1s(d2)$ must be included in Eq. (4.4-4) in order to represent the dissociation to form two "1s" hydrogen atoms as $R \to \infty$. 
Using the wavefunctions given by Eqs. (4.4-3) and (4.4-4) respectively for $H_2^+$ and $H_2$ and solving the secular equations, Eq. (4.3-18), the minimum value of $\tilde{E}$ is obtained by varying the screening constants, $\eta$, of the STO's and the position(s) of the expansion centre(s) (that is $\rho$ or $\rho_a$ and $\rho_b$). The variational procedures are discussed in Appendix F. The nuclear attraction and Coulomb integrals occurring in the calculations were evaluated by using a computer program written and supplied by Todd\textsuperscript{124}. These integrals have been checked by using other programs written by Janiszewski and Wahl\textsuperscript{102} and by Kouba\textsuperscript{125}. The nuclear attraction integrals of the form, $\int \chi_{n\ell}^m (cl) \chi_{n'\ell'}^{m'} (cl) r_{al} dr$, involving orbitals through h type STO's have also been checked by using the closed form expressions given by Lofthus\textsuperscript{126}. The Coulomb integrals involving orbitals up to 2p STO's have also been checked by using the closed form expressions of Roothaan\textsuperscript{101}.

4.4B RESULTS AND DISCUSSION FOR $H(1s)$-$H^+$

Calculations for the ground state energy of $H_2^+$ using the basis set $\{1s\}, \{1s,2s\}, \{1s,2s,2p\}$ and $\{1s,2s,3d\}$ were first carried out for $1 \leq R \leq 18$ a. u. to initiate the search for a suitable basis set. The ratios, $R$, defined by Eq. (4.1-1),
\[ R = \frac{E_{ab}}{E_{ab}}^{\text{exact}} \]  \hfill (4.4-7)

for these calculations are shown as functions of \( R \) in

Fig. (4.4-1). The results corresponding to the larger basis
sets, \{1s,2s,2p\} and \{1s,2s,3d\}, show a shallow minimum
near \( R = 6 \, a_0 \) and suggest that one can expect basis sets
which give good results at this particular value of \( R \) will
give reasonably good results for intermediate and large \( R \)
as well. Thus assuming, for the present, that the minimum
persists as the number of configurations increases, one can
investigate the rate of convergence to the exact energy as
a function of the number and kind of configurations in the
basis set by calculating the energy near \( R = 6 \, a_0 \).

To proceed with the search for a suitable basis set
which is efficient and economical in the sense of conver-
gence, a systematic set of calculations was done at \( R = 6 \, a_0 \)
using basis sets containing \( s, \, p \) and \( d \) type STO's. The
results of these calculations are reported in Table (4.4-1)
and lead to the following observations:

1) Including more than one orbital having the same azimuthal
quantum number \( \ell \) in the basis set does not, in general,
change the floating parameter \( \rho \) (the change, if any,
is not significant) and does not lead to a significant
Fig. (4.4-1) Comparison of the interaction energy calculated from the floating one centre method, using various basis sets, with the corresponding exact results for ground state $H_2^+$ as a function of $R$. \[ \mathcal{R} = \frac{\bar{E}_{ab}}{E_{ab} \text{ (exact)}} \]
Table (4.4-1) Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of the basis size for the $H(1s)$-$H^+$ interaction at $R = 6$ $a_0$. The basis sets are constructed from $s$, $p$ and $d$ type STO's only; $E_{ab}$ (exact) = $-0.1197(-1)$ $\text{112}$. The value of $\rho$ is given as "zero" when it is less than $10^{-4}$ $a_0$.

<table>
<thead>
<tr>
<th>Group</th>
<th>Configurations Included</th>
<th>$\tilde{E}_{ab}$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1s$</td>
<td>0.2906(-3)</td>
<td>0.22(-1)</td>
</tr>
<tr>
<td></td>
<td>$1s,2s$</td>
<td>0.2913(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s$</td>
<td>0.2918(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,3d$</td>
<td>0.4539(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3d$</td>
<td>0.4550(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,3d$</td>
<td>0.4551(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,3d,4d$</td>
<td>0.4578(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,3d,4d,5d$</td>
<td>0.4584(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,3d,4d$</td>
<td>0.4564(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,3d,4d,5d$</td>
<td>0.4574(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3d,4d$</td>
<td>0.4575(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3d,4d,5d$</td>
<td>0.4579(-3)</td>
<td>&quot;</td>
</tr>
<tr>
<td>2</td>
<td>$1s,2p$</td>
<td>0.1789(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,2p$</td>
<td>0.1800(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p$</td>
<td>0.1800(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p,3p$</td>
<td>0.1813(-2)</td>
<td>0.1(-2)</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p,3p,4p$</td>
<td>0.1814(-2)</td>
<td>0.1(-2)</td>
</tr>
<tr>
<td></td>
<td>$1s,2p,3p$</td>
<td>0.1802(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2p,3p,4p$</td>
<td>0.1805(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,2p,3p$</td>
<td>0.1813(-2)</td>
<td>0.1(-2)</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,2p,3p,4p$</td>
<td>0.1814(-2)</td>
<td>0.1(-2)</td>
</tr>
<tr>
<td>3</td>
<td>$1s,2p,3d$</td>
<td>0.2139(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,2p,3d$</td>
<td>0.2166(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,2p,3p,3d,4d$</td>
<td>0.2177(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p,3p,3d,4d$</td>
<td>0.2186(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p,3p,4p,3d,4d$</td>
<td>0.2187(-2)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$1s,2s,3s,2p,3p,3d,4d,5d$</td>
<td>0.2187(-2)</td>
<td>0</td>
</tr>
</tbody>
</table>
improvement (less than or equal to 1% for the calculations shown in Table (4.4-1)) in the calculated energies. However adding a new orbital of different $\ell$ value to the basis set will give a more significant improvement in the energy.

2) Basis sets with only orbitals of even $\ell$ values tend to float the expansion centre off the nucleus. Once orbitals with odd $\ell$ values appear in a basis set the floating of the expansion centre is greatly reduced (the floating parameter becomes zero in most cases); compare results of Group (1) with Groups (2) and (3) in Table (4.4-1). That is the orbitals with even $\ell$ values tend to float the expansion centre off the nucleus while the orbitals with odd $\ell$ values tend to keep the centre close to the nucleus.

The first point suggests that to test the rate of convergence as a function of the number of configurations in the floating centre(s) method one can increase the

---

* The improvement in energy may be more significant if one adds a very large number of orbitals of the same $\ell$ value to the basis set. This is apparently true for $R = 2 \, a_0$ where the expansion centre is at the internuclear midpoint, see Refs. (113,127) and (115).
number of configurations in a basis set by adding a single orbital of different \( l \) value to the spherical core \([1s,2s]\). The results for this test are given in Table (4.4-2) and one sees that convergence to the exact value of \( E_{ab} \) is very slow as a function of \( l \) for the calculations considered here. This is not hard to rationalize. For small \( R \) where the expansion centre is at the internuclear midpoint, the convergence as a function of \( l \) has been shown\(^{23,24}\) very slow and the energy increment becomes proportional to \( l^{-4} \) as \( l \) becomes large \((l \geq 16)\)\(^{26,104}\). For large \( R \), where the expansion centre is at a nucleus, the energy increment is proportional\(^{40}\) to \( R^{-2}(l+1) \).

The second point can be investigated further by calculating the interaction energies using basis sets consisting of orbitals with even \( l \) values only and with odd \( l \) values only in addition to the 1s core orbital. The results obtained by using the even \( l \) basis set, \([1s,3d,5g,7i]\), and the odd \( l \) basis set, \([1s,2p,4f,6h]\), are given in Table (4.4-3) as a function of \( R \) and the different characteristics of the two basis sets can be seen by comparing the floating parameters for them. The orbitals with odd \( l \) values tend to stay close to the nucleus since they give zero contribution to the energy if centred at the internuclear midpoint for the ground state \( \text{H}_2^+ \) molecule. In the calculations
Table (4.4-2) Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of $\ell$ for the H(1s)--$H^+$ interaction at $R = 6 \text{ a}_0$. The basis sets are constructed from STO's through $\ell = 6$. $E_{ab}$ (exact) = $-0.1197(-1)$.  

<table>
<thead>
<tr>
<th>Configurations Included*</th>
<th>$\rho$</th>
<th>$\tilde{E}_{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s,2s</td>
<td>0.22(-1)</td>
<td>0.2907(-3)</td>
</tr>
<tr>
<td>1s,2s,2p</td>
<td>0</td>
<td>0.1789(-2)</td>
</tr>
<tr>
<td>1s,2s,2p,3d</td>
<td>0</td>
<td>0.2139(-2)</td>
</tr>
<tr>
<td>1s,2s,2p,3d,4f</td>
<td>0</td>
<td>0.2292(-2)</td>
</tr>
<tr>
<td>1s,2s,2p,3d,4f,5g</td>
<td>0</td>
<td>0.2387(-2)</td>
</tr>
<tr>
<td>1s,2s,2p,3d,4f,5g,6h</td>
<td>0</td>
<td>0.2455(-2)</td>
</tr>
<tr>
<td>1s,2s,2p,3d,4f,5g,6h,7i</td>
<td>0</td>
<td>0.2506(-2)</td>
</tr>
</tbody>
</table>

* In this calculation and all subsequent calculations the same screening constants are used for the 1s and 2s orbitals.
Table (4.4-3)  Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ calculated from basis sets containing a $\{1s\}$ core and even or odd $t$ orbitals only as a function of $R$ for the $H(1s)-H^+$ interaction. The exact interaction energies $E_{ab}^{\text{exact}}$ are also given for comparison.

| $R$ | Basis Set | \begin{array}{c|c|c|c}
|     | $\tilde{E}_{ab}$ & $\rho$ & $\tilde{E}_{ab}$ & $\rho$
| \hline
| 2   | {1s,3d,5g,7i} | 0.3069 (-1) & 0.172 (-1) & 0.2820 (-1) & 0.1026 (0)
| 3   | {1s,2p,4f,6h} | 0.6537 (-2) | 0  | 0.2045 (-1) & 0.7756 (-1)
| 4   | {1s,3d,5g,7i} | 0.2776 (-2) | 0  | 0.9201 (-2) & 0.4608 (-1)
| 5   | {1s,2p,4f,6h} | 0.1108 (-2) | 0  | 0.3991 (-2) & 0.2442 (-1)
| 6   | {1s,3d,5g,7i} | 0.4782 (-3) | 0  | 0.1884 (-2) & 0.1197 (-1)
| 8   | {1s,2p,4f,6h} | 0.1242 (-3) | 0  | 0.5671 (-3) & 0.2570 (-2)
| 10  | {1s,3d,5g,7i} | 0.4562 (-4) | 0  | 0.2276 (-3) & 0.5787 (-3) |
involving orbitals with even $l$ values only, the orbitals tend to float off the nucleus for $R \geq 3 \ a_0$ in order to give some characteristics of the orbitals with odd $l$ values$^{116}$. For example, the off centre is orbital, when expanded about the proton, will have some characteristics of a proton centred 2p orbital$^{115}$ which is very important for the calculation of the long range interaction energy (see below).

To investigate the convergence of the floating centre(s) method as a function of the number of configurations at internuclear separations other than $R = 6 \ a_0$, the interaction energy was calculated by using several different basis sets for $2 \leq R \leq 10 \ a_0$. The ratios, $R$, obtained from these calculations are shown as functions of $R$ in Fig. 4.4-1 and the convergence to the exact results as a function of the number of configurations for all $R$ is in general very slow. These results also show that the 2p and 3d orbitals are especially important for large and small $R$ respectively. For large $R$ where the expansion centre is at a nucleus the 2p orbital gives the lead term for the long range energy$^{40}$ while for small $R$ the expansion centre goes to the internuclear midpoint where the 2p orbital gives no contribution and hence the 3d orbital is very important.
The variation of $\rho$ as a function of $R$ and $\ell$, corresponding to the basis sets indicated in Fig. (4.4-1), is illustrated in Fig. (4.4-2). The effect of adding orbitals with even $\ell$ values to a basis set can be seen by comparing the curves corresponding to the basis sets $\{1s\}$, $\{1s,2s\}$ and $\{1s,2s,3d\}$. The effect of adding orbitals with odd $\ell$ values to a basis set can be seen by comparing the following curves: $\{1s\}$ with $\{1s,2p\}$, $\{1s,2s\}$ with $\{1s,2s,2p\}$, and $\{1s,2s,3d\}$ with $\{1s,2s,3d,2p\}$.

The ratios, $R$, obtained by using basis sets, $\{1s,2s,2p\}$ and $\{1s,2s,2p,3d,4f,5g,6h,7i\}$ with the expansion centre at $\rho = 0$, $\rho = R/2$ and optimized $\rho$ ($\rho_{op}$), are shown as a function of $R$ in Fig. (4.4-3) to demonstrate some features of the floating one centre method. The relationship between the floating one centre method and the fixed one centre method (fixed at the internuclear midpoint or at a nucleus) discussed in Sec. 4.3 is illustrated in this figure. That is the $\rho = R/2$ and $\rho = 0$ results join the $\rho_{op}$ results for small and large $R$ respectively and the $\rho_{op}$ calculations give reasonably good results for all $R$ while the $\rho = R/2$ and the $\rho = 0$ results behave badly for large and moderate small $R$ respectively. The importance of allowing the expansion centre to float rather than being fixed at $\rho = 0$ or $\rho = R/2$ is clearly basis set dependent. This can be seen in Fig. (4.4-3) by comparing
Fig. (4.4-2) Optimal values of the floating parameter $\rho$, for various basis sets, as a function of $R$ for ground state $H_2^+$. 

- $\{1s\}$
- $\{1s,2s\}$
- $\{1s,2s,2p\}$
- $\{1s,2s,2p,3d\}$
- $\{1s,2s,2p,3d,4f,5g\}$
- and
- $\{1s,2s,2p,3d,4f,5g,6h,7i\}$
Fig. (4.4-3) Comparison of the interaction energy obtained from the basis sets \([1s,2s,2p]\) and \([1s,2s,2p,3d,4f,5g,6h,7i]\), for various choices of the expansion centre, with the corresponding exact results for ground state \(H_2^+\) as a function of \(R\). \(R = \frac{E_{ab}}{E_{ab\text{ (exact)}}} \).
the $\rho = 0$, $\rho = R/2$ and $\rho = \rho_{op}$ results for the basis set $[1s,2s,2p]$ with the corresponding results for the "larger" basis set $[1s,2s,2p,3d,4f,5g,6h,7i]$. From these comparisons it is clear that the "floating" is very important for a "larger" basis set as well as for a "smaller" basis set. The numerical results for the interaction energy of the ground state $H_2^+$ molecule obtained from the largest basis set used in this work are summarized in Table (4.4-4) as a function of $R$.

The floating centre method has also been used by Tamássy-Lentei and Bába$^{118}$ to calculate the ground state energy of the $H_2^+$ molecule for $R \leq 3.6 \ a_0$. They used simple basis sets constructed from $1s$, $2s$, $2p$ and $3d$ hydrogen like atomic orbitals for their calculations and concluded that floating the expansion centre was useful only for the minimal $[1s]$ basis set calculations. These authors found that results equivalent to the floating centre results could be obtained from the superposition of the $\rho = 0$ and the $\rho = R/2$ calculation. This is confirmed by the present more sophisticated floating centre calculations; see Fig. (4.4-3) where the superposition of the $\rho = 0$ and $\rho = R/2$ results essentially duplicates the $\rho_{op}$ results. However it is important to realize that in order to know that the superposition of the $\rho = 0$ and $\rho = R/2$ results
Table (4.4-4) Optimum values for the floating parameter \( \rho \) and screening constants \( \eta \) and the interaction energy \( \tilde{E}_{ab} \) as a function of \( R \) when the basis set \{1s,2s,2p,3d,4f,5g,6h,7i\} is used in the variational calculations of the \( H(1s) - H^+ \) interaction.

<table>
<thead>
<tr>
<th>R</th>
<th>( \rho )</th>
<th>( \eta )</th>
<th>( \tilde{E}_{ab} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.0</td>
<td>1.610 2.205 4.033 6.073</td>
<td>0.8873(-1)</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>1.281 1.602 2.753 4.074</td>
<td>0.4901(-1)</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.95 0.74 0.87 1.04 1.23 1.45 1.67</td>
<td>0.1729(-1)</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.99 0.71 0.72 0.80 0.92 1.05 1.19</td>
<td>0.2506(-2)</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0.99 0.76 0.71 0.72 0.77 0.86 0.96</td>
<td>0.6329(-3)</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>1.00 0.77 0.74 0.72 0.73 0.77 0.83</td>
<td>0.2402(-3)</td>
</tr>
</tbody>
</table>
are essentially equivalent to the $\rho_{op}$ results one must actually perform the floating centre calculations for the energy.

The fixed one centre method for ground state $H_2^+$ with the expansion centre at the internuclear midpoint and at one of the protons has been studied by Dvoraček and Horák\textsuperscript{28} for $1 \leq R \leq 9$ a$_0$ and by Hauk, Kim, Parr and Hemaka\textsuperscript{29} for $0.2 \leq R \leq 8$ a$_0$. These authors have suggested that the reason for the misbehaviour of the midpoint centre calculations for large R is the inability of the midpoint centre wavefunction to describe the localization of the electron about a proton. However they were not able to explain the behaviour of their proton centre calculations as R becomes large satisfactorily. These problems and the results for all R obtained from the fixed one centre calculations are easily understood by the present floating one centre approach. With a proper choice of configurations in the variational basis set for the $H_2^+$ molecule, the midpoint centre calculations can give good results for small R since the method can yield the exact united atom treatment\textsuperscript{29,107,115} as $R \to 0$; see Sec. 4.3A. The proton centre calculations can give good results for large R since the method yields the exact long range treatment\textsuperscript{40} and describes the dissociation
properly as $R \rightarrow \infty$; see also Sec. 4.3A. Since the $\rho = 0$
calculations neglect electron exchange effects, the results
represent the Coulomb energy for the ground $1s\sigma_g$ state of
$H_2^+$ and therefore agree with the average energy of the $1s\sigma_g$
and $2p\sigma_u$ states of $H_2^+$ as $R$ becomes large, see also Ref.
(115).

It must be pointed out here that the present
discussions on the floating one centre method are for
molecules like $H_2^+$ which dissociate to a "bare" nucleus
and an atom. For molecules which dissociate to give two
species, both of which contain electron(s), the one centre
(fixed or floating) approach can not be used and modifications
have to be made to the method, see Sec. 4.2. Discussions
using the ground state $H_2$ molecule as an example will be
given in the next section.

4.4C RESULTS AND DISCUSSION FOR $H(1s)-H(1s)$

The sequence of calculations for the ground state $H_2$
molecule is analogous to that for the ground state $H_2^+$
molecule discussed in Sec. 4.4B. Here the configurations
used for the calculations, which are defined in Eqs. (4.4-5)
and (4.4-6), are simply represented by $(n,\ell)^2$ and $(n,\ell)(n',\ell')$
where $(n,\ell)^2$ represents $[(n,\ell,0)(n,\ell,0)]$ and $[(n,\ell,+1)(n,\ell,-1)]$
and $(n,\ell)(n',\ell')$ represents $[(n,\ell,0)(n',\ell',0)]$ and
\[(n, l, +1)(n', l', -1)]\].

A systematic set of calculations carried out at \(R = 6 \, a_0\) by using basis sets consisting of configurations constructed in a "lexicographic" like order from \(s, p\) and \(d\) type STO's is reported in Table (4.4-5). The configurations of the form \((n, 0)(n' \neq n, l')\), see Eq. (4.4-4), are neglected in the calculations performed at \(R = 6 \, a_0\) in order to reduce the size of the secular equation to be solved since these terms do not yield a significant improvement in the calculated energy. For example at \(R = 6 \, a_0\)

adding the configuration \((1s2s)\) to the basis set \([1s^2, 2s^2]\) only gives a 0.1% energy increment while adding the configurations \((1s2p)\) and \((1s3d)\) to the basis set \([1s^2, 2p^2, 2p3d, 3d^2]\) gives less than an 0.5% energy increment. However it should be noted that adding the configurations \((1s2p)\) and \((1s3d)\) to the basis set \([1s^2, 2p^2, 2p3d, 3d^2]\) gives energy increments of 2.4, 7.4 and 23.7 per cent for \(R = 5, 4\) and \(3 \, a_0\) respectively. On the other hand adding the configuration \((1s2s)\) to the basis set \([1s^2, 2s^2]\) only gives an 0.2% energy increment at \(R = 4 \, a_0\).

The results in Table (4.4-5) indicate that including configurations of the form, \((n, l)(n', l')\) with \(n > l + 1\)
Table (4.4-5) Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of the basis set size for the $H(1s)-H(1s)$ interaction at $R = 6 \, \text{a}_0$. The basis sets are constructed from the $s$, $p$ and $d$ type STO's only. $E_{ab}^{\text{exact}} = -0.8150 \times 10^{-3}$. 

<table>
<thead>
<tr>
<th>Configurations Included</th>
<th>$\tilde{E}_{ab}$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^2$</td>
<td>$0.5974 \times 10^{-4}$</td>
<td>$0.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>$1s^2,2s^2$</td>
<td>$0.6017 \times 10^{-4}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,3s^2$</td>
<td>$0.6053 \times 10^{-4}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2p^2$</td>
<td>$0.1764 \times 10^{-3}$</td>
<td>$0.16 \times 10^{-3}$</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2$</td>
<td>$0.1769 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,3p^2$</td>
<td>$0.1778 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2\mu^2,2p3p$</td>
<td>$0.1783 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,2p3p,3p^2$</td>
<td>$0.1784 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,3p^2,4p^2$</td>
<td>$0.1800 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2p^2,2p3d$</td>
<td>$0.2200 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,2p3d,3p^2$</td>
<td>$0.2239 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,2p3d,3p^2,3p3d$</td>
<td>$0.2244 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s^2,2s^2,2p^2,2p3d,3p^2,3p3d,4p^2,5p^2$</td>
<td>$0.2248 \times 10^{-3}$</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
and \( n' \geq \ell' + 1 \) or vice versa, for given values of \( \ell \) and \( \ell' \), does not change the floating parameter \( \rho = \rho_a = \rho_b \) or improve the calculated energy significantly compared with the results obtained by adding configurations with new values of \( \ell \) and/or \( \ell' \). Thus to test the rate of convergence as a function of the number of configurations used in the trial wavefunction of Eq. (4.4-4), we consider calculations using the configurations, \((n, \ell) (n', \ell')\) with \( n = \ell + 1 \) and \( n' = \ell' + 1 \) for given values of \( \ell \) and \( \ell' \). The results for this test, using basis sets consisting of configurations constructed in a lexicographic type order using orbitals through \( \ell, \ell' = 3 \), are given in Table (4.4-6) for \( R = 4 \) and \( 6 \, a_0 \). In these test calculations, the configurations, \((1, 0) (n', \ell')\) with \( n' = \ell' + 1 \) and \( \ell' \leq 2 \) are included in the basis sets since they are important for \( R < 6 \, a_0 \). The configuration \((1s4f)\) and configurations of the form \((n, \ell) (n', \ell')\) with \(|m|, |m'| \geq 2\), are neglected in the basis sets in order to reduce the size of the secular equation. The \((1s4f)\) configuration is not important for long range interactions and gives zero contribution for small \( R \) where the expansion centre is at the internuclear

\[ \dagger \] These terms are also relatively unimportant at small \( R \) where the expansion centres are at the internuclear midpoint, see Ref. (103).
Table (4.4-6) Values for the interaction energy $\tilde{E}_{ab}$ and the floating parameter $\rho$ as a function of $\ell$ for the H(1s)--H(1s) interaction at $R = 4$ and 6 a$_0$. The basis sets are constructed from STO's through $\ell = 3$. $E_{ab}$ (exact) is from Ref. (90a).

<table>
<thead>
<tr>
<th>Configurations Included</th>
<th>$R = 4$ a$<em>0$ $E</em>{ab}$ (exact) = $-0.1637(-1)$</th>
<th>$R = 6$ a$<em>0$ $E</em>{ab}$ (exact) = $-0.8150(-3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_{op}$</td>
<td>$\tilde{E}_{ab}$</td>
</tr>
<tr>
<td>$1s^2$</td>
<td>0.26(-2)</td>
<td>0.1634(-2)</td>
</tr>
<tr>
<td>$1s^2,1s2p,2p^2$</td>
<td>0</td>
<td>0.2377(-2)</td>
</tr>
<tr>
<td>$1s^2,1s2p,2p^2,1s3d,2p3d,3d^2$</td>
<td>0</td>
<td>0.2844(-2)</td>
</tr>
<tr>
<td>$1s^2,1s2p,2p^2,1s3d,2p3d$</td>
<td>0</td>
<td>0.2976(-2)</td>
</tr>
<tr>
<td>$3d^2,2p4f,3d4f,4f^2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
midpoint. The configurations with $|m|, |m'| \geq 2$ do not connect with configurations constructed from orbitals of lower $\ell$ and/or $\ell'$ values which can only have $|m|, |m'| < 2$. For example adding the configurations $(3d_{\pm 2})^2$ to the basis set $\{1s^2, 2p^2, 2p3d, 3d^2\}$ only gives an energy increment of 0.1% at $R = 6 \; a_0$ and adding the configurations $(3d_{\pm 2})^2 \ (3d_{\pm 2} \ 4f_{\pm 2})^2 \ (4f_{\pm 2})^2$ to the basis set $\{1s^2, 2p^2, 2p3d, 3d^2, 2p4f, 3d4f, 4f^2\}$ yields 0.2% and 0.4% energy increments at $R = 6$ and $4 \; a_0$ respectively. The numerical results obtained from the largest basis set used in this work for the calculation of the ground state interaction energy of $H_2$ are summarized in Table (4.4-7) as a function of $R$.

The results corresponding to the basis sets listed in Table (4.4-6) have also been calculated for $1 \leq R \leq 10 \; a_0$. The ratios, $R$, obtained from these results are shown as a function of $R$ in Fig. (4.4-4). The convergence to the exact results for the interaction energy is very slow as a function of $\ell$ for all $R$. This is not hard to rationalize since for small $R$, where the expansion centres coalesce at the internuclear midpoint, the energy increment has been shown to be very small as a function of $\ell$ and is proportional to $\ell^{-4}$ as $\ell$ becomes large while for large $R$, where the expansion centres are located at the
Table (4.4-7) Optimum values for the floating parameter $\rho$ and screening constants $\eta$ and the interaction energy $\tilde{E}_{ab}$ as a function of $R$ when the basis set $\{1s^2, 1s2p, 2p^2, 1s3d, 2p3d, 3d^2, 2p4f, 3d4f, 4f^2\}$ is used in the variational calculations of the $H(1s)-H(1s)$ interaction. The exact interaction energies, $E_{ab}$ (exact), are given for comparison.

<table>
<thead>
<tr>
<th>R</th>
<th>$\rho$</th>
<th>$\eta$</th>
<th>$\tilde{E}_{ab}$</th>
<th>$E_{ab}$ (exact)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1s</td>
<td>2p</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td></td>
<td>1.12</td>
<td>1.75</td>
</tr>
<tr>
<td>1.2</td>
<td>0.21(-1)</td>
<td></td>
<td>1.04</td>
<td>1.35</td>
</tr>
<tr>
<td>1.4</td>
<td>0.8(-2)</td>
<td></td>
<td>1.00</td>
<td>1.23</td>
</tr>
<tr>
<td>1.6</td>
<td>1.0</td>
<td></td>
<td>0.97</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td></td>
<td>0.94</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td></td>
<td>0.97</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td></td>
<td>0.99</td>
<td>1.03</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td></td>
<td>0.999</td>
<td>0.941</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td></td>
<td>1.000</td>
<td>0.889</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td></td>
<td>1.000</td>
<td>0.868</td>
</tr>
</tbody>
</table>
Fig. (4.4-4) Comparison of the interaction energy calculated from the floating two centre method, using various basis sets, with the corresponding exact results for ground state H\textsubscript{2} as a function of R. \( R = \frac{E_{ab}}{E_{ab\text{ (exact)}}} \).
two nuclei, the increment is proportional to $R^{-2(l+l'+1)}$. One also sees from Fig. (4.4-4) that for small $R$ the configurations $(1s2p)$ and $(2p^2)$ and the configurations $(1s3d)$, $(2p3d)$ and $(3d^2)$ are nearly of equal importance while for large $R$ the $2p$ orbitals are especially important. For large $R$ the $2p$ orbitals give the $R^{-6}$ lead term for the long range energy $^{2,10,32}$.

The interaction energy, as a function of $R$, has been calculated by using the basis sets, \{1s^2,2p^2\} and \{1s^2,2p^2,2p3d,3d^2,2p4f,3d4f,4f^2\} with the expansion centres at $\rho_a = \rho_b = \rho = 0$, $\rho_a = \rho_b = \rho = R/2$ and $\rho_a = \rho_b = \rho = \rho_{op}$. These results are used to calculate the corresponding ratios, $R$, as a function of $R$ which are shown in Fig. (4.4-5). The relationship between the floating two centre method and the fixed centre(s) methods (i.e. the one centre, $\rho = R/2$, calculations and the two centre, $\rho = 0$, calculations) can be clearly seen in Fig. (4.4-5). That is the $\rho = R/2$ and $\rho = 0$ results join the $\rho_{op}$ results for small and large $R$ respectively. These results show that the superposition of the $\rho = R/2$ and $\rho = 0$ results is not equivalent to the $\rho_{op}$ results for some values of $R$. The importance of floating the two expansion centres rather than fixing them at $\rho = 0$ or $\rho = R/2$ is also clearly seen in this figure. Comparing the $\rho = 0$, $\rho = R/2$ and $\rho = \rho_{op}$ results for the
Fig. (4.4-5) Comparison of the interaction energy obtained from the basis sets \([1s^2, 2p^2]\) and \([1s^2, 2p^2, 2p3d, 3d^2, 2p4f, 3d4f, 4f^2]\), for various choices of the expansion centres, with the exact results for ground state \(H_2\) as a function of \(R\).

\[
R = \frac{\tilde{E}_{ab}}{E_{ab}(\text{exact})}
\]
basis set \{1s^2,2p^2\} with the corresponding results for the "larger" basis set \{1s^2,2p^2,2p3d,3d^2,2p4f,3d4f,4f^2\}, one can see that the "floating" is important for a "larger" basis set as well as for a "smaller" basis set.

It should be noted that the results for H_2 depend markedly on the type of configurations included in the basis sets. This is illustrated in Fig. (4.4-6) where the ratio \( R \) corresponding to the \{1s^2,1s2p,2p^2\} and \{1s^2,1s2p,2p^2,1s3d,2p3d,3d^2,2p4f,3d4f,4f^2\} basis sets are given as a function of \( R \) for various choices of the expansion centres. Here one sees that in the superposition of the \( \rho = R/2 \) and \( \rho = 0 \) results the \( \rho = 0 \) calculations alone can almost reproduce the \( \rho_{\text{opt}} \) results for all \( R \) and the "floating" of the two centres is minimal when the configuration (1s2p) is added to the basis set \{1s^2,2p^2\} and configurations (1s2p) and (1s3d) are added to the basis set \{1s^2,2p^2,2p3d,3d^2,2p4f,3d4f,4f^2\}. The reason that the \( \rho = 0 \) results for H_2 are good for all \( R \) is that a properly chosen two centre (\( \rho = 0 \)) wavefunction, even without electron exchange, is undoubtedly better than a single centre wavefunction to describe a two centre system for all \( R \). It is important to realize however, that to have two floating centres is always very important with respect to the \( \rho = R/2 \) calculations for obtaining reasonable results.
Fig. (4.4-6) Comparison of the interaction energy obtained from the basis sets \( \{1s^2, 1s2p, 2p^2\} \) and \( \{1s^2, 1s2p, 2p^2, 1s3d, 2p3d, 3d^2, 2p4f, 3d4f, 4f^2\} \), for various choices of the expansion centres, with the exact results for ground state \( \text{H}_2 \) as a function of \( R \). \( \mathcal{R} = \frac{\tilde{E}_{ab}}{E_{ab} \text{(exact)}} \).
for all \( \mathbf{R} \) and is important as well in the understanding of the one centre method as \( \mathbf{R} \) increases from its equilibrium separation.

4.5 **GENERAL DISCUSSION OF THE CONVERGENCE OF THE FLOATING CENTRE(S) METHOD FOR THE MODEL GROUND STATE \( \text{H}(1s) - \text{H}^+ \) AND \( \text{H}(1s) - \text{H}(1s) \) INTERACTIONS**

The model floating centre(s) calculations for the ground state energies of \( \text{H}_2^+ \) and \( \text{H}_2 \) are very slowly convergent with respect to the exact results for all except very small and large values of \( \mathbf{R} \). It is clear that one of the problems with the method is associated with the fact that, in the model calculations presented here, the optimized expansion centres are located at the proton(s) until \( \mathbf{R} \) becomes relatively small\(^\dagger\). Hence for most values of \( \mathbf{R} \) the calculated energies converge, at most, to the total Coulomb energies\(^5-7\) and not to the total energies including electron exchange effects. For the ground state \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules the Coulomb energy is dominant\(^5,18,47,90a,112\) with respect to the exchange energy only for large values of \( \mathbf{R} \).

\(^\dagger\) The discussion here is only valid for our more sophisticated calculations, namely the calculations which include configurations in the basis sets that will yield proper long range results for large \( \mathbf{R} \). For the calculations using basis functions with even \( \ell \) values only the expansion centre remains off the proton for fairly large values of \( \mathbf{R} \), see Sec. 4.4B.
The failure of the energy optimized floating centre(s) to float off the protons in the calculations for the ground state $\text{H}_2^+$ and $\text{H}_2$ molecules can be understood by considering two competitive effects. Namely the need to satisfy the cusp condition $^{23,25,113,114}$ at the two protons while simultaneously building up the charge distribution between the protons to reproduce electron exchange effects. Let us consider the floating centre(s) method from the viewpoint of large $R$. For the $\text{H}_2^+$ molecule, which contains two protons "a" and "b" and only one electron, the single centre wavefunction can not represent the cusps at the two protons symmetrically unless the expansion centre is at the internuclear midpoint. For a given finite basis set, floating the expansion centre away from proton "a" towards the internuclear midpoint will yield a poorer representation of the cusp at "a" while increasing the charge distribution between "a" and "b" and the charge distribution near "b". For the $\text{H}_2$ molecule, which contains two electrons, the floating two centre wavefunction represents the cusps symmetrically at the two protons for all $R$. For a given finite basis set floating the expansion centres away from the two protons towards the internuclear midpoint will yield a poorer representation of the two cusps near the protons while the charge distribution between the protons is
increased. It is clear that in order to obtain good results from the floating centre(s) calculations one must somehow satisfy these two competitive effects simultaneously. The present model calculations indicate that, on an energy criterion, the satisfaction of the cusp condition is more important than increasing the charge distribution between the protons for all except small R. For very small R the expansion centre is at the internuclear midpoint, the cusps at the protons and the charge distribution between the protons can be well represented simultaneously by using a large single centre basis set\textsuperscript{25,106}, see also Table (4.1-1).

In order to satisfy the two competitive effects discussed above for intermediate values of R one must find wavefunctions which can float off the proton(s) and well represent the two cusps simultaneously. However it should be pointed out that even if these wavefunctions can be found there is still a problem associated with the floating one centre treatment of H\textsubscript{2}\textsuperscript{+}. That is the one centre wavefunction for the ground state of H\textsubscript{2}\textsuperscript{+} does not have g symmetry if the expansion centre is not located at the internuclear midpoint. Katriel\textsuperscript{129}, see also Ref. (115), has pointed out that once the expansion centre has shifted from the internuclear midpoint the one centre wavefunction becomes a mixed wavefunction of g and u symmetries. For example, consider the extreme
case where the expansion centre is at one of the protons. Here one obtains an approximation to the Coulomb energy which is the same for the ground \( 1s_g \) and the first excited \( 2p_u \) states of \( \text{H}_2^+ \). Therefore the mixing of symmetries has no effect on the calculated Coulomb results. Also, it is clear\(^{25,26,105,106}\) that the calculated results represent the total energy for the \( 1s_g \) state of \( \text{H}_2^+ \) when the expansion centre is located at the internuclear midpoint. When the expansion centre is located between a proton and the internuclear midpoint the floating centre method will probably\(^{130}\) yield an approximation to the total energy. However since for these values of \( R \) the wavefunction is of mixed symmetry the convergence to the energy of the ground \( 1s_g \) state will be very slow.

In the one centre midpoint calculations for the ground state energies of \( \text{H}_2^+ \) and \( \text{H}_2 \), several authors have shown that the use of basis sets constructed from Slater type orbitals with non-integer principle quantum numbers\(^{106,108,109}\) and/or high principle quantum numbers\(^{104a,111}\) can accelerate the convergence of the method. Here two very simple tests are performed by using these two kinds of basis sets in an attempt to float the expansion centre(s) off the proton(s). The floating one centre basis set \([ns,n'p,n''d]\) with energy optimized non-integer quantum numbers \( n, n' \) and \( n'' \) and the
floating two centre basis set \{1s^2,2p^2,10p^2\} are used to calculate the ground state energies for the \( \text{H}_2^+ \) and \( \text{H}_2 \) molecules respectively at \( R = 6 \ a_0 \). The result for \( \text{H}_2^+ \) obtained by using the basis set \{ns,n'p,n''d\} only gives a 1% energy increment over the \{1s,2p,3d\} basis set with the expansion centre remaining at a proton. The result for \( \text{H}_2 \) obtained by using the basis set \{1s^2,2p^2,10p^2\} gives an 8% energy increment over the \{1s^2,2p^2,3p^2\} basis set with the expansion centres again remaining at the two protons. The results for these two calculations are summarized in Table (4.5-1). These results suggest that the two kinds of basis sets tested here may not be useful in floating the expansion centre(s) off the proton(s) for intermediate values of \( R \). However the significant improvement in energy shown by using high principle quantum number basis set for \( \text{H}_2 \) indicates that this type of basis set may be very useful in obtaining Coulomb energies for intermediate values of \( R \).
Table (4.5-1) The interaction energies and the optimum values for the variational parameters in the basis sets \{ns, n'p, n''d\} and \{1s^2, 2p^2, 10p^2\} used for the calculations of ground state energies for H_2^+ and H_2 respectively at R = 6 a_0.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>H_2^+</th>
<th>H_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis set</td>
<td>{ns, n'p, n''d}</td>
<td>{1s^2, 2p^2, 10p^2}</td>
</tr>
<tr>
<td>(\rho = 0)</td>
<td>(\rho = 0)</td>
<td></td>
</tr>
<tr>
<td>(n = 0.998)</td>
<td>(\eta_{1s} = 1.000)</td>
<td></td>
</tr>
<tr>
<td>Variational Parameters</td>
<td>(n' = 2.256)</td>
<td>(\eta_{2p} = 0.952)</td>
</tr>
<tr>
<td>(n'' = 3.966)</td>
<td>(\eta_{10p} = 1.130)</td>
<td></td>
</tr>
<tr>
<td>(\eta_{ns} = 0.991)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\eta_{n'p} = 0.842)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\eta_{n''d} = 1.017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tilde{E}_{ab})</td>
<td>0.2159(-2)</td>
<td>0.1956(-3)</td>
</tr>
</tbody>
</table>
5. CONCLUSIONS

Strictly speaking the $R^{-1}$ series expansion for intermolecular forces is an asymptotic representation for the part of total Coulomb energy which possesses an asymptotic expansion for large $R$. It is not an asymptotic representation for the total Coulomb energy until $R$ is sufficiently large so that the exponential part of the total Coulomb energy is negligible, see Secs. 2.1C and 2.3A. In Chapter 2 the dependence of the asymptotic behaviour of the $R^{-1}$ series on the nature of interacting species is investigated. In Sec. 2.3 the divergent nature of the asymptotic $R^{-1}$ series is shown to become apparent at much larger internuclear separation for bonded or excited state interactions than for non-bonded interactions in agreement with the fact that neglect of charge overlap effects is responsible for the divergence of the series. For most interactions only the leading or at most the first few terms of the $R^{-1}$ series are known accurately. Furthermore the convergence of the series is very slow for intermediate values of $R$. Thus the direct use of the $R^{-1}$ series is limited in two ways. The asymptotic nature of the series limits its usefulness for "small" values of $R$, while
the slow rate of convergence of the series limits its usefulness for "intermediate" values of R. In Sec. 2.4 the Padé approximation method is shown to be a simple useful way to remove some of the difficulties associated with the slow rate of convergence of the $R^{-1}$ series. It should be emphasized however that the method does not alleviate the problem associated with the asymptotic divergent nature of the series. Indeed the Padé approximations probably give a very realistic indication of the asymptotic nature of the intermolecular force series.

In Chapter 3 the modified generalized Brillouin-Wigner perturbation theory in the Unsöld's approximation is shown to be an effective way to incorporate charge overlap and exchange effects into the long range treatment of intermolecular forces for moderately large $R$ where accurate variational results are usually not available. This approach also eliminates the difficulties of evaluating the matrix elements of $H^2$ and $H^3$ that arise in the usual Unsöld's treatments, see Secs. 3.1B and 3.1C. This modified perturbation technique will be very useful for excited states where charge overlap effects persist for large values of $R$. Finally it appears the interaction energies for the $^3\pi_g$, $^1\pi_g$ and $^3\pi_u$ states of $H_2$, obtained from the modified perturbation treatments, are probably the best representations of the potential energy
curves for these states presently available for $R \geq 8 \, a_0$.

In Chapter 4 the floating centre(s) method is formally shown to be capable of extending the (fixed) one centre method to intermediate and large values of $R$. The method, for all $R$, retains the basic features of the long range treatment of intermolecular forces including charge overlap effects and therefore reproduces the proper long range behaviour of the interaction as a function of $R$. Thus one of the problems in the one centre midpoint calculations for homonuclear diatomic molecules has been resolved. However the calculations for the ground state energies of $H_2^+$ and $H_2$ show the convergence of the floating centre(s) approach can be very slow for all but very large or very small values of $R$. In order to speed up the convergence for these ground state calculations for intermediate values of $R$ one must find wavefunctions which can float off the proton(s) and represent the two cusps at the protons simultaneously. It is important to realize that even if these wavefunctions can be found there is still a symmetry problem associated with the calculations for the ground state $H_2^+$ molecule, see Sec. 4.5.

Several authors $^{25,113,131-133}$ have pointed out that the (fixed) one centre (midpoint) method is more suitable for the excited states of the $H_2^+$ and $H_2$ molecules than for
their ground states. This is because\textsuperscript{23,113,131-133} the excited state molecules have smaller cusps at the protons which are easier to represent by using a finite one centre basis set. One can undoubtedly anticipate that the floating centre(s) method will also yield better results for the excited states of these molecules than for their corresponding ground states. Also the floating centre(s) method can yield good representations of the Coulomb energy when the floating centre(s) remain at the proton(s), see Sec. 4.5. It would be very interesting to investigate the excited states of \( \text{H}_2^+ \) and \( \text{H}_2 \) and other molecules whose energies are Coulomb dominated by the floating centre(s) method.
APPENDIX A. THE SEPARATION OF $E^{(2)}_{\text{res}}$ OF SEC. 2.1C INTO INDUCTION AND DISPERSION ENERGIES

In Sec. 2.1C the resonant part of the second order energy, $E^{(2)}_{\text{res}}$, is given by Eq. (2.1-31). This equation can be decomposed\textsuperscript{10} into three terms depending on various choices of $u''$ and $u'''$ to give

$$E^{(2)}_{\text{res}} = -2 \sum_{u'' \neq u'} \frac{\langle \phi_a \phi_b | V | \phi_a \phi_{b'} \rangle \langle \phi_a \phi_b | V | \phi_a \phi_{b''} \rangle}{\varepsilon_a(v) + \varepsilon_b(v'') - \varepsilon^{(0)}}$$

$$- 2 \sum_{u'' \neq u} \frac{\langle \phi_a \phi_b | V | \phi_a \phi_b \rangle \langle \phi_a \phi_{b'} | V | \phi_a \phi_{b''} \rangle}{\varepsilon_a(v) + \varepsilon_b(v') - \varepsilon^{(0)}}$$

$$- \sum_{u'' \neq u, u'} \frac{\langle \phi_a \phi_b | V | \phi_a \phi_{b'} \rangle \langle \phi_a \phi_b | V | \phi_a \phi_{b''} \rangle}{\varepsilon_a(v') + \varepsilon_b(v'') - \varepsilon^{(0)}} \quad . \quad (A-1)$$

In Eq. (A-1), one may consider the first two terms as non-expanded induction energies and the third term as a non-expanded dispersion energy. However, in some ways this is not very meaningful since the structures of these terms are
quite different from the usual non-expanded induction or
dispersion energies; compare the first two terms of Eq.
(A-1) with (2.1-24) and the third term of Eq. (A-1) with
Eq. (2.1-25). This can be made clearer by substituting
the multipole expansion of \( V \) into the corresponding
equations. For example, substituting Eqs. (2.2-2)-(2.2-4)
for \( V \) into the first term of Eq. (A-1), one obtains in the
configuration space of molecule "a" the integral;

\[
\mathbf{I} = \langle \varphi_a^{(u)} | Q_{a}^{(a)} | \varphi_a^{(w)} \rangle \langle \varphi_a^{(u)} | Q_{a}^{(a)} | \varphi_a^{(w)} \rangle . \tag{A-2}
\]

Eq. (A-2) corresponds to the product of a permanent moment
and a transition moment while the corresponding result for
the usual expanded induction energy is a product of two
permanent moments.\(^{2,10,37}\).
APPENDIX B. THE MIXING OF 1s2s AND 1s2p_σ CONFIGURATIONS FOR THE H(1s)-H(n=2) INTERACTION

The mixing of the 1s2s and 1s2p_σ configurations has been neglected in Sec. 2.3A with respect to the study of the charge overlap effects in the H(1s)-H(2s) interaction. Here the importance of this mixing is investigated by an application of first order degenerate perturbation theory^9,100 to Eq. (2.1-2) for the H(1s)-H(n=2) interactions. It is easy to show that only the 1s2s and 1s2p_σ configurations mix in this problem.

The zeroth order wavefunction \( \Psi^{(0)} \) is given by^36,56

\[
\Psi^{(0)} = C_1 \Psi_1^{(0)} + C_2 \Psi_2^{(0)}
\]  \hspace{1cm} (B-1)

where for the \( ^1\Sigma_g^+ \left( ^3\Sigma_u^+ \right) \) state

\[
\Psi_1^{(0)} = 2^{-\frac{1}{2}} \left[ |s_\alpha^{(1)} s_b^{(2)} + 2s_\alpha^{(1)} s_b^{(2)} \right] 
\]

\[
\Psi_2^{(0)} = 2^{-\frac{1}{2}} \left[ |s_\alpha^{(1)} p_{\sigma b}^{(2)} - 2p_{\sigma \alpha}^{(1)} s_b^{(2)} \right] 
\]  \hspace{1cm} (B-2)

while for the \( ^1\Sigma_u^+ \left( ^3\Sigma_g^+ \right) \) state
\[
\Psi_1^{(o)} = 2^{-\frac{1}{2}} \left[ |s_{\alpha}^{(o)} \right. \left. 2s_{\beta}^{(o)} - 2s_{\alpha}^{(o)} |s_{\beta}^{(o)} \right]
\]

\[
\Psi_2^{(o)} = 2^{-\frac{1}{2}} \left[ |s_{\alpha}^{(o)} 2p_{\sigma}^{(o)} + 2p_{\sigma}^{(o)} |s_{\beta}^{(o)} \right] \quad (B-2')
\]

\(\psi_1^{(o)}\) and \(\psi_2^{(o)}\) are the wavefunctions for the pure \(1s2s\) and \(1s2p\) configurations which do not mix when the multipole expansion of \(V\) is used, see Sec. 2.3A.

After the wavefunctions, \(\psi_1^{(o)}\) and \(\psi_2^{(o)}\), for the state of interest \([^1\Sigma_g^+ (^3\Sigma_u^+)\) or \([^1\Sigma_u^+ (^3\Sigma_g^+)\)] are selected for \(\psi^{(o)}\), the two solutions for the first order energy, \(E_+^{(1)}\) and \(E_-^{(1)}\), are given by

\[
E_+^{(o)} = \frac{1}{2} \left[ (V_{11} + V_{22}) \pm \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2} \right] \quad (B-3)
\]

where

\[
V_{ij} = \langle \psi_i^{(o)} | V | \psi_j^{(o)} \rangle \quad i, j = 1, 2 \quad (B-4)
\]

The integrals \(V_{ij}\), where \(V\) is given by Eq. (2.3-2), can be decomposed into integrals which are available from Refs. (101,134) and are therefore easily evaluated. The solutions for the coefficients of mixing \(C_1\) and \(C_2\), are given by
$$C_{1\pm} = \left\{ \frac{V_{21}}{2 |V_{21}|} \left[ 1 \pm \frac{V_{11} - V_{22}}{\sqrt{(V_{11} - V_{22})^2 + 4 |V_{12}|^2}} \right] \right\}^{1/2}$$  \hspace{1cm} (B-5)$$

$$C_{2\pm} = \pm \left\{ \frac{V_{21}}{2 |V_{12}|} \left[ 1 \pm \frac{V_{11} - V_{22}}{\sqrt{(V_{11} - V_{22})^2 + 4 |V_{12}|^2}} \right] \right\}^{1/2}$$  \hspace{1cm} (B-6)$$

Here the upper and lower signs correspond to the two solutions of the first order energy, $E_+^{(1)}$ and $E_-^{(1)}$ respectively. Since $V_{12} = V_{21}$ one obtains from Eqs. (B-5) and (B-6) the following relations;

$$C_{1+} = - C_{2-}$$

$$C_{2+} = C_{1-}$$  \hspace{1cm} (B-7)$$

The first order energies, $E_+^{(1)}$ and $E_-^{(1)}$, and the coefficients, $C_{1-}$ and $C_{2-}$ are given for $R = 2(2)16$ a$_0$ in Tables (B.1) and (B.2) for the $^1\Sigma_g^+ (^3\Sigma_u^+)$ and $^1\Sigma_u^+ (^3\Sigma_g^+)$ states respectively. The first order energies corresponding to the pure 1s2s and 1s2p$\sigma$ configurations,

$$E_{1s2s}^{(1)} = V_{11}$$  \hspace{1cm} (B-8)$$

and

$$E_{1s2p\sigma}^{(1)} = V_{22}$$
Table B.1 \( ^1\Sigma_g^+ (^3\Sigma_u^+) \) states of \( \text{H}_2 \). First order energies and coefficients of mixing for the \( 1s2s \) and \( 1s2p_\sigma \) configurations. The first order energies for the pure configurations are given for comparison.

<table>
<thead>
<tr>
<th>R</th>
<th>( C_{1-} )</th>
<th>( C_{2-} )</th>
<th>(-E^{(1)}_{-})</th>
<th>(-E^{(1)}_{1s2s})</th>
<th>( E^{(1)}_{+})</th>
<th>( E^{(1)}<em>{1s2p</em>\sigma})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.3263</td>
<td>-0.9453</td>
<td>0.4037(-2)</td>
<td>-0.2984(-1)</td>
<td>0.3388(-1)</td>
<td>-0.1870(-5)</td>
</tr>
<tr>
<td>4</td>
<td>0.5933</td>
<td>-0.8050</td>
<td>0.1984(-1)</td>
<td>0.4134(-2)</td>
<td>0.4398(-2)</td>
<td>-0.1131(-1)</td>
</tr>
<tr>
<td>6</td>
<td>0.7334</td>
<td>-0.6798</td>
<td>0.6754(-2)</td>
<td>0.2693(-2)</td>
<td>0.2034(-2)</td>
<td>-0.2027(-2)</td>
</tr>
<tr>
<td>8</td>
<td>0.8669</td>
<td>-0.4985</td>
<td>0.1546(-2)</td>
<td>0.8620(-3)</td>
<td>0.1206(-2)</td>
<td>0.5220(-3)</td>
</tr>
<tr>
<td>10</td>
<td>0.9676</td>
<td>-0.2523</td>
<td>0.2863(-3)</td>
<td>0.2151(-3)</td>
<td>0.8332(-3)</td>
<td>0.7619(-3)</td>
</tr>
<tr>
<td>12</td>
<td>0.9959</td>
<td>-0.0905</td>
<td>0.5208(-4)</td>
<td>0.4692(-4)</td>
<td>0.5786(-3)</td>
<td>0.5734(-3)</td>
</tr>
<tr>
<td>14</td>
<td>0.9996</td>
<td>-0.0275</td>
<td>0.9697(-5)</td>
<td>0.9394(-5)</td>
<td>0.3918(-3)</td>
<td>0.3915(-3)</td>
</tr>
<tr>
<td>16</td>
<td>0.9999</td>
<td>-0.0075</td>
<td>0.1786(-5)</td>
<td>0.1771(-5)</td>
<td>0.2686(-3)</td>
<td>0.2686(-3)</td>
</tr>
</tbody>
</table>
Table (B.2) $^1\Sigma_u^+ (^3\Sigma_g^+)$ states of H$_2$. First order energies and coefficients of mixing for the 1s2s and 1s2p$_\sigma$ configurations. The first order energies for the pure configurations are given for comparison.

<table>
<thead>
<tr>
<th>R</th>
<th>$C_{1-}$</th>
<th>$C_{2-}$</th>
<th>$-E^{(1)}_-$</th>
<th>$-E^{(1)}<em>{1s2p</em>\sigma}$</th>
<th>$-E^{(1)}_+$</th>
<th>$-E^{(1)}_{1s2s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.7055</td>
<td>-0.7087</td>
<td>0.2502 (1)</td>
<td>-0.3667 (-2)</td>
<td>-0.2517 (1)</td>
<td>-0.1848 (-1)</td>
</tr>
<tr>
<td>4</td>
<td>0.6559</td>
<td>-0.7548</td>
<td>0.7668 (-1)</td>
<td>0.2110 (-1)</td>
<td>-0.5251 (-1)</td>
<td>0.3068 (-2)</td>
</tr>
<tr>
<td>6</td>
<td>0.1049</td>
<td>-0.9945</td>
<td>0.9413 (-2)</td>
<td>0.9332 (-2)</td>
<td>0.2023 (-2)</td>
<td>0.2104 (-2)</td>
</tr>
<tr>
<td>8</td>
<td>0.0297</td>
<td>-0.9996</td>
<td>0.3496 (-2)</td>
<td>0.3494 (-2)</td>
<td>0.7518 (-3)</td>
<td>0.7542 (-3)</td>
</tr>
<tr>
<td>10</td>
<td>0.0667</td>
<td>-0.9978</td>
<td>0.1433 (-2)</td>
<td>0.1428 (-2)</td>
<td>0.1957 (-3)</td>
<td>0.2012 (-3)</td>
</tr>
<tr>
<td>12</td>
<td>0.0420</td>
<td>-0.9991</td>
<td>0.7098 (-3)</td>
<td>0.7086 (-3)</td>
<td>0.4427 (-4)</td>
<td>0.4545 (-4)</td>
</tr>
<tr>
<td>14</td>
<td>0.0168</td>
<td>-0.9999</td>
<td>0.4173 (-3)</td>
<td>0.4172 (-3)</td>
<td>0.9141 (-5)</td>
<td>0.9256 (-5)</td>
</tr>
<tr>
<td>16</td>
<td>0.0</td>
<td>-1.0</td>
<td>0.2733 (-3)</td>
<td>0.2733 (-3)</td>
<td>0.1759 (-5)</td>
<td>0.1759 (-5)</td>
</tr>
</tbody>
</table>
are also given in the Tables for comparison. It should be pointed out that, for the $^1\Sigma_g^+$ ($^3\Sigma_u^+$) state the lower root of the first order energy, $E_{-}^{(1)}$, corresponds to the state of this symmetry which dissociates to give H(1s) and H(2s) atoms since $C_{1-} \rightarrow 1$, $C_{2-} \rightarrow 0$ as $R \rightarrow \infty$ while the higher root, $E_{+}^{(1)}$, corresponds to the state of the same symmetry which dissociates to give H(1s) and H(2p) atoms since $C_{1+} \rightarrow 0$, $C_{2+} \rightarrow 1$ as $R \rightarrow \infty$. However for the $^1\Sigma_u^+$ ($^3\Sigma_g^+$) state $E_{-}^{(1)}$ corresponds to the state of this symmetry which dissociates into a H(1s) and a H(2p) atom since $C_{1-} \rightarrow 0$, $C_{2-} \rightarrow -1$ as $R \rightarrow \infty$ while $E_{+}^{(1)}$ corresponds to the state of the same symmetry which dissociates into H(1s) and H(2s) atoms since $C_{1+} \rightarrow 1$, $C_{2+} \rightarrow 0$ as $R \rightarrow \infty$. 
APPENDIX C. THE EVALUATION OF THE NON-EXPANDED UNSÖLD'S SECOND ORDER INTERACTION ENERGIES FOR THE H(1s)–H(2s) INTERACTION

The Unsöld's second-order Coulomb interaction energies given in Eqs. (2.3-3)–(2.3-7) for the H(1s)–H(2s) interaction are evaluated using the non-expanded interaction potential energy, $V$, given by Eq. (2.3-2).

C.1 DISCUSSION OF THE EVALUATION OF THE BASIC INTEGRALS DEFINED IN SEC. (C.2)

The basic integrals occurring in the model interaction energies for the H(1s)–H(2s) interaction, see Sec. (C.4), are listed in Sec. (C.2) and explicit expressions for them are given in Sec. (C.3).

From the fact that the hydrogen atom 2s orbitals, $\hat{a}$ or $\hat{b}$, are linear combination of Slater 1s and 2s orbitals, the one electron integrals denoted by $I_1$ through $I_6$ are available as sums of integrals from Coulson\textsuperscript{134} or Roothaan\textsuperscript{101} either directly or by differentiating with respect to screening constants in their results. The two electron integrals, $I_7$ and $I_8$, are available from Roothaan\textsuperscript{101}. 
Integrals I₉, I₁₀ and I₁₁ are evaluated by a technique similar to that used to evaluate the two centre Coulomb integral, \( \langle a^2(1) | \frac{1}{r_{12}} | b^2(2) \rangle \), given by Slater. Integrals I₁₂ and I₁₃ can be obtained either by using the method of Milleur, Twerdochlib and Hirschfelder or by differentiating their results for \( \langle a^2(1) | \frac{1}{r_{12}} | b^2(2) \rangle \) with respect to screening constants in \( a(1) \) and \( b(2) \).

It should be pointed out that the integrals given by Coulson which contain a logarithmic term should have the argument of the logarithm enclosed in absolute value signs.

### C.2 INTEGRAL LIST FOR THE MODEL CALCULATIONS OF THE H(1s)–H(2s) INTERACTION OF SEC. 2.3A

The following one and two electron integrals are used in the evaluation of Coulomb energies for the model calculations of the H(1s)–H(2s) interaction discussed in Sec. 2.3A.

\[
I_1 = \langle a_\omega \mid a_\omega \rangle = \langle \hat{a}_\omega \mid \hat{a}_\omega \rangle \\
I_2 = \langle a_\omega \mid \frac{1}{r_{12}} \mid a_\omega \rangle \\
I_3 = \langle \hat{a}_\omega \mid \frac{1}{r_{12}} \mid \hat{a}_\omega \rangle \\
I_4 = \langle a_\omega \mid \frac{1}{r_{1b1}} \mid \hat{a}_\omega \rangle \\
I_5 = \langle a_\omega \mid \frac{1}{r_{1b1}} \mid a_\omega \rangle \\
I_6 = \langle \hat{a}_\omega \mid \frac{1}{r_{1b1}} \mid \hat{a}_\omega \rangle \\
I_7 = \langle a_\omega \hat{b}_\omega \mid \frac{1}{r_{12}} \mid a_\omega \hat{b}_\omega \rangle \\
I_8 = \langle a_\omega b_\omega \mid \frac{1}{r_{12}} \mid \hat{a}_\omega \hat{b}_\omega \rangle \\
I_9 = \langle a_\omega \hat{b}_\omega \mid \frac{1}{r_{1b1}} \mid a_\omega \hat{b}_\omega \rangle \\
I_{10} = \langle a_\omega \hat{b}_\omega \mid \frac{1}{r_{1b1}} \mid a_\omega \hat{b}_\omega \rangle \\
I_{11} = \langle a_\omega b_\omega \mid \frac{1}{r_{1a2}} \mid \hat{a}_\omega \hat{b}_\omega \rangle \\
I_{12} = \langle a_\omega \hat{b}_\omega \mid \frac{1}{r_{1a2}} \mid a_\omega \hat{b}_\omega \rangle \\
I_{13} = \langle a_\omega b_\omega \mid \frac{1}{r_{1a2}} \mid \hat{a}_\omega \hat{b}_\omega \rangle
\]
C.3 EXPLICIT EXPRESSIONS FOR THE INTEGRALS LISTED IN (C.2)

\[ I_1 = 1 \]

\[ I_2 = \frac{1}{R} - \left( \frac{1}{R} + 1 \right) e^{-2R} \]

\[ I_3 = \frac{1}{R} - \left( \frac{1}{R} + \frac{3}{4} + \frac{R}{4} + \frac{R^2}{8} \right) e^{-R} \]

\[ I_4 = 2^{\frac{-\gamma}{2}} \left( \frac{8}{27} + \frac{4R}{9} \right) e^{-3R/2} \]

\[ I_5 = \left( 1 + \frac{1}{2R} \right) e^{-2R} E_i(2R) + \left( 1 - \frac{1}{2R} \right) e^{2R} E_i(-2R) \]

\[ I_6 = \left( -\frac{1}{8R} + \frac{1}{8} + \frac{R}{16} + \frac{R^2}{16} \right) e^{R} E_i(-R) \]

\[ + \left( \frac{1}{8R} + \frac{1}{8} - \frac{R}{16} + \frac{R^2}{16} \right) e^{-R} E_i(R) \]

\[ I_7 = \frac{1}{R} + \left( \frac{128}{81R} - \frac{76}{27} + \frac{4R}{9} - \frac{2R^2}{9} \right) e^{-R} - \left( \frac{5}{9} + \frac{209}{81R} \right) e^{2R} \]

\[ I_8 = \left( \frac{16}{729} + \frac{8R}{243} + \frac{4R^2}{243} - \frac{R^4}{405} \right) e^{-3R/2} \]

\[ I_9 = \left( -\frac{49}{54R} + \frac{1}{9} - \frac{R}{12} \right) e^{-2R} + \left( \frac{49}{54R} - \frac{11}{12} + \frac{R}{2} - \frac{R^2}{24} \right) e^{-R} \]

\[ - \left( \frac{1}{8R} + \frac{1}{8} - \frac{R}{16} + \frac{R^2}{16} \right) e^{-R} \ln 3 \]

\[ + \left( -\frac{1}{8R} + \frac{1}{8} + \frac{R}{16} + \frac{R^2}{16} \right) e^{R} E_i(-R) \]
\[ I_{10} = \left( \frac{26}{27R} + \frac{28}{27} \right) e^{-2R} \left( \frac{26}{27R} - \frac{4}{27} + \frac{2R}{9} \right) e^{-R} - \left( 1 + \frac{1}{2R} \right) e^{-2R} \ln 3 \]
\[ + \left( \frac{1}{2R} - 1 \right) e^{2R} E_i(-3R) - \left( \frac{1}{2R} + 1 \right) e^{-2R} E_i(R) \]
\[ - \left( \frac{1}{2R} - 1 \right) e^{2R} E_i(-2R) + \left( \frac{1}{2R} + 1 \right) e^{-2R} E_i(2R) \]

\[ I_{11} = \left( \frac{28}{729} + \frac{14R}{243} - \frac{2R^2}{243} - \frac{R^3}{162} \right) e^{-3R/2} \]

\[ I_{12} = \frac{8}{9} + \left( \frac{5}{9} - \frac{373}{162R} \right) e^{2R} E_i(-2R) + \left( \frac{5}{9} + \frac{373}{162R} \right) e^{-2R} E_i(2R) \]
\[ + \left( \frac{178}{81R} + \frac{50}{27} + \frac{5R}{9} + \frac{R^2}{9} \right) e^{R} E_i(-R) \]
\[ + \left( - \frac{178}{81R} + \frac{50}{27} - \frac{5R}{9} + \frac{R^2}{9} \right) e^{-R} E_i(R) \]

\[ I_{13} = \frac{152}{10935} + \frac{8R^2}{1215} - \left( \frac{8}{729R} - \frac{4}{243} + \frac{R^2}{81} - \frac{R^3}{162} - \frac{R^4}{540} \right) e^{3R/2} E_i(-3R/2) \]
\[ + \left( \frac{8}{729R} + \frac{4}{243} - \frac{R^2}{81} - \frac{R^3}{162} + \frac{R^4}{540} \right) e^{-3R/2} E_i(3R/2) \]
C.4 THE NON-EXPANDED SECOND ORDER ENERGIES IN UNSÖLD'S APPROXIMATION FOR THE \( \text{H}(1s) - \text{H}(2s) \) INTERACTION OF SEC. 2.3A

The non-expanded second-order energy for the model \( \text{H}(1s) - \text{H}(2s) \) interaction in the Unsöld's approximation can be expressed in terms of the basic integrals listed in Sec. (C.2). The upper and lower signs correspond to the \( ^1\Sigma_g^+ (^3\Sigma_u^+) \) and \( ^1\Sigma_u^+ (^3\Sigma_g^+) \) states respectively.

\[
\tilde{E}^{(2)} = - \frac{1}{\Delta} \left\{ \frac{1}{R^2} + I_5 + I_6 + I_{12} + 2 (I_2 I_3 - I_4 - I_{10}) \\
+ \frac{2}{R} (I_7 - I_2 - I_3) \pm (I_{13} - 4 I_{11} + 2 I_4 + \frac{2}{R} I_8) \\
- \left( E^{(1)} \right)^2 \right\}
\]  
(C.4-1)

where

\[
E^{(1)} = \frac{1}{R} + I_7 - I_2 - I_3 \pm I_8
\]  
(C.4-2)

This second order energy can be decomposed into \( \tilde{E}^{(2)}_{R-1} \) and \( \tilde{E}^{(2)}_{\exp(-R)} \), see Sec. (2.1C), which are given in closed form by
\[ \tilde{E}_{R^{-1}}^{(a)} \Delta = -\frac{8}{9} + \frac{152}{10935} - \frac{1}{R^2} + \frac{8R^2}{1215} \]

\[ -\left( \frac{1505}{648R} - \frac{373}{216} + \frac{71R}{144} + \frac{7R^2}{144} \right) e^R E_i(-R) \]

\[ +\left( \frac{1505}{648R} + \frac{373}{216} + \frac{71R}{144} - \frac{7R^2}{144} \right) e^{-R} E_i(R) \]

\[ -\left( \frac{318}{81R} + \frac{32}{9} \right) e^{-2R} E_i(2R) + \left( \frac{318}{81R} - \frac{32}{9} \right) e^{2R} E_i(-2R) \]

\[ \mp \left( \frac{8}{729R} + \frac{4}{243} - \frac{R^2}{81} - \frac{R^3}{162} + \frac{R^4}{540} \right) e^{3R/2} E_i(-3R/2) \]

\[ \mp \left( \frac{8}{729R} + \frac{4}{243} - \frac{R^2}{81} - \frac{R^3}{162} + \frac{R^4}{540} \right) e^{-3R/2} E_i(3R/2) \quad (C.4-3) \]

\[ \tilde{E}_{exp(-R)}^{(a)} \Delta = \left( \frac{418}{81R^2} + \frac{11}{9R} + \frac{62}{27} + \frac{R}{6} \right) e^{-2R} \]

\[ -\left( \frac{256}{81R^2} - \frac{149}{27R} + \frac{131}{54} - R + \frac{R^2}{12} \right) e^{-R} \]

\[ -\left( \frac{2}{R^2} + \frac{7}{2R} + 2 + \frac{3R}{4} + \frac{R^2}{4} \right) e^{-3R} \]

\[ \mp \left( \frac{64}{729} + \frac{64R}{243} + \frac{16R^2}{81} \right) e^{-3R} \]

\[ \mp \left( \frac{80}{729} + \frac{40R}{243} + \frac{16R^2}{243} - \frac{4R^3}{162} + \frac{2R^4}{405} \right) e^{-3R/2} \]

\[ -\left( \frac{1}{4R} + \frac{1}{4} - \frac{R}{8} + \frac{R^2}{8} \right) e^{-R} \ln 3 \quad (C.4-4) \]

\[ -\left( \frac{1}{4R} + \frac{1}{4} + \frac{R}{8} + \frac{R^2}{8} \right) e^{R} E_i(-3R) \]
\[-\left(\frac{1}{4R} + \frac{1}{4} - \frac{R}{8} + \frac{R^2}{8}\right)e^{-R}E_i(-R)\]
\[-\left(\frac{1}{R} + 2\right)e^{-2R}\ln 3 + \left(\frac{1}{R} - 2\right)e^{2R}E_i(-3R)\]
\[-\left(\frac{1}{R} + 2\right)e^{-2R}E_i(R) + \left(E''\right)^2\]

The first order energy occurring in Eq. (C.4-4) can be written, see Sec. 2.1C, as

\[E'' = E''_{dir} \pm E''_{res}\]  \hspace{1cm} (C.4-5)

where

\[E''_{dir} = \left(\frac{209}{81R} - \frac{223}{108} + \frac{25R}{36} - \frac{7R^2}{72}\right)e^{-R} + \left(\frac{1}{R} + 1\right)e^{-2R}\]  \hspace{1cm} (C.4-6)

\[E''_{res} = \left(\frac{16}{729} + \frac{8R}{243} + \frac{4R^2}{243} - \frac{R^4}{405}\right)e^{-3R/2}\]  \hspace{1cm} (C.4-7)

The second order energy, Eq. (C.4-1), can also be decomposed into \(\bar{E}_{dir}^{(2)}\) and \(\bar{E}_{res}^{(2)}\), see Sec. 2.1C, which are given by,

\[\bar{E}_{dir}^{(2)} = -\frac{8}{9} - \frac{1}{R^4}\]
\[-\left(\frac{1505}{648R} - \frac{373}{216} + \frac{71R}{144} + \frac{7R^2}{144}\right)e^R E_i(-R)\]
\[+\left(\frac{1505}{648R} + \frac{373}{216} + \frac{71R}{144} - \frac{7R^2}{144}\right)e^{-R} E_i(R)\]
\[-\left(\frac{318}{81R} + \frac{32}{9}\right)e^{-2R}E_i(2R) + \left(\frac{318}{81R} - \frac{32}{9}\right)e^{2R}E_i(-2R)\]

\[-\left(\frac{256}{81R} - \frac{149}{27R} + \frac{131}{54} - R + \frac{R^2}{12}\right)e^{-R}\]

\[+ \left(\frac{418}{81R^2} + \frac{11}{9R} + \frac{62}{27} + \frac{R}{6}\right)e^{-2R}\]

\[-\left(\frac{R}{4} + \frac{3}{4} + 2 + \frac{7}{2R} + \frac{2}{R^2}\right)e^{-3R}\]

\[-\left(\frac{1}{4R} + \frac{1}{4} - \frac{R}{8} + \frac{R^2}{8}\right)e^{-R}\ln 3\]

\[-\left(-\frac{1}{4R} + \frac{1}{4} + \frac{R}{8} + \frac{R^2}{8}\right)e^{R}E_i(-3R)\]

\[-\left(\frac{1}{4R} + \frac{1}{4} - \frac{R}{8} + \frac{R^2}{8}\right)e^{-R}E_i(-R)\]

\[-\left(\frac{1}{R} + 2\right)e^{-2R}\ln 3 + \left(\frac{1}{R} - 2\right)e^{2R}E_i(-3R)\]

\[-\left(\frac{1}{R} + 2\right)e^{-2R}E_i(R) + \left(E_{dir}^{(1)}\right)^2\]  

(C.4-8)

\[\bar{E}_{res}^{(2)} \Delta = -\frac{152}{10935} - \frac{8R^2}{1215}\]

\[-\left(-\frac{8}{729R} + \frac{4}{243} - \frac{R^2}{81} + \frac{R^3}{162} + \frac{R^4}{540}\right)e^{3R/2}E_i\left(-\frac{3R}{2}\right)\]

\[-\left(\frac{8}{729R} + \frac{4}{243} - \frac{R^2}{81} - \frac{R^3}{162} + \frac{R^4}{540}\right)e^{-3R/2}E_i\left(\frac{3R}{2}\right)\]

\[-\left(\frac{16R^2}{81} + \frac{64R}{243} + \frac{64}{729}\right)e^{-R}\]

\[+\left(\frac{80}{729} + \frac{40R}{243} - \frac{16R^2}{243} - \frac{4R^3}{162} + \frac{2R^4}{405}\right)e^{-3R/2}\]

\[\pm \left(E_{res}^{(1)}\right)^2 + 2E_{res}^{(1)}E_{dir}^{(1)}\]  

(C.4-9)
APPENDIX D. THE EVALUATION OF THE EXPANDED UNSÖLD'S
SECOND ORDER INTERACTION ENERGIES FOR THE
H(1s)-H(2s) INTERACTION

The Unsöld's expansion coefficients, \( \tilde{c}_{2m}^{(2)} \) (direct) and
\( \tilde{c}_{2m}^{(2)} \) (resonance), given by Eqs. (2.3-10) and (2.3-11) in
Sec. 2.3, are easily obtained from Appendix C by neglecting
all the terms decreasing exponentially with increasing \( R \)
and using the asymptotic expansion\(^{59,137}\) for the functions,
\( e^{cR}E_i(-cR) \) and \( e^{-cR}E_i(cR), c > 0, \) in Eqs. (C.4-8) and (C.4-9).

\[
\begin{align*}
E_i(-cR) &= -\frac{1}{cR} \sum_{n=0}^{\infty} \frac{(-1)^n n!}{(cR)^n} \\
E_i(cR) &= \frac{1}{cR} \sum_{n=0}^{\infty} \frac{n!}{(cR)^n}
\end{align*}
\] (D-1) (D-2)

The same results\(^{17}\) for the Unsöld's coefficients can
also be obtained by using the multipole expansion of the
interaction potential \( V \) given by Eqs. (2.2-2)-(2.2-6) in
Eqs. (2.3-4) and (2.3-5). This procedure has been carried
out and the results used to check Eqs. (2.3-10) and (2.3-11).
APPENDIX E. THE MIXING OF $1s2s$ AND $1s2p_\sigma$ CONFIGURATIONS, INCLUDING ELECTRON EXCHANGE, FOR THE $a^3\Sigma^+_g$ STATE OF $H(1s)-H(n=2)$ INTERACTION

The procedures to find the first order energies and the proper zeroth order wavefunctions from the two degenerate configurations are discussed in Appendix B when electron exchange effects are neglected. If the electron exchange effects are to be included, the properly antisymmetrized wavefunctions for the degenerate configurations must be used for $\psi_1^{(0)}$ and $\psi_2^{(0)}$ in Eq. (B-1). That is the antisymmetrized wavefunctions corresponding to the pure $3\Sigma^+_g(1s,2s)$ and pure $3\Sigma^+_g(1s,2p_\sigma)$ states, see Eq. (3.3-1) and Table (3.3-1), are used for $\psi_1^{(0)}$ and $\psi_2^{(0)}$ respectively.

All integrals involved in the calculations were evaluated by using the computer program "MINT1"\textsuperscript{102}. Results for the first order energies, $E_-^{(1)}$ and $E_+^{(1)}$, and the coefficients of mixing, $C_{1-}$ and $C_{2-}$, see Appendix B, are given for $R = 2(2)16$ $a_0$ in Table (E.1) for the relevant $3\Sigma^+_g$ states of $H_2$. The effects of electron exchange on the mixing can be seen by comparing results in Table (E.1) with the corresponding results in Table (B.2).
Table E.1  $^3\Sigma_g^+$ states of $\text{H}_2$. First order energies and coefficients of mixing for the 1s2s and 1s2p configurations including electron exchange. The first order energies, $E^{(1)}_{1s2s}$ and $E^{(1)}_{1s2p}$, obtained by using antisymmetrized wavefunctions for pure configurations are given for comparison.

<table>
<thead>
<tr>
<th>R</th>
<th>$C_{1^-}$</th>
<th>$C_{2^-}$</th>
<th>$-E^{(1)}_-$</th>
<th>$-E^{(1)}_{1s2p\sigma}$</th>
<th>$E^{(1)}_+$</th>
<th>$E^{(1)}_{1s2s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.9999</td>
<td>-0.0029</td>
<td>0.7169 (-1)</td>
<td>-0.3125 (0)</td>
<td>0.3125 (0)</td>
<td>-0.7169 (-1)</td>
</tr>
<tr>
<td>4</td>
<td>0.9772</td>
<td>-0.2124</td>
<td>0.2339 (-1)</td>
<td>-0.6092 (-1)</td>
<td>0.6490 (-1)</td>
<td>-0.1940 (-1)</td>
</tr>
<tr>
<td>6</td>
<td>0.8555</td>
<td>-0.5179</td>
<td>0.3183 (-2)</td>
<td>-0.1645 (-1)</td>
<td>0.2365 (-1)</td>
<td>0.4013 (-2)</td>
</tr>
<tr>
<td>8</td>
<td>0.7437</td>
<td>-0.6685</td>
<td>0.9836 (-3)</td>
<td>-0.3726 (-2)</td>
<td>0.7533 (-2)</td>
<td>0.2823 (-2)</td>
</tr>
<tr>
<td>10</td>
<td>0.6167</td>
<td>-0.7872</td>
<td>0.5693 (-3)</td>
<td>-0.3277 (-3)</td>
<td>0.1789 (-2)</td>
<td>0.8920 (-3)</td>
</tr>
<tr>
<td>12</td>
<td>0.3744</td>
<td>-0.9273</td>
<td>0.4340 (-3)</td>
<td>0.3276 (-3)</td>
<td>0.3253 (-3)</td>
<td>0.2189 (-3)</td>
</tr>
<tr>
<td>14</td>
<td>0.1368</td>
<td>-0.9906</td>
<td>0.3487 (-3)</td>
<td>0.3412 (-3)</td>
<td>0.5449 (-4)</td>
<td>0.4695 (-4)</td>
</tr>
<tr>
<td>16</td>
<td>0.0391</td>
<td>-0.9992</td>
<td>0.2594 (-3)</td>
<td>0.2590 (-3)</td>
<td>0.9631 (-5)</td>
<td>0.9219 (-5)</td>
</tr>
</tbody>
</table>
From Table (E.1) it is easy to see that the lower root, $E_1^{(1)}$, corresponds to the $a_1^3 \Sigma^+$ state of $H_2$ which dissociates into $1s$ and $2p_0$ H atoms\textsuperscript{138} when $R$ becomes large.
APPENDIX F. THE VARIATIONAL PROCEDURE

The set of variational parameters which gives the lowest possible value of the energy $\tilde{E}$ in the floating centre(s) calculations of the $H_2^+$ and $H_2$ molecules discussed in Secs. 4.3B and 4.4 are found by the "Pattern Search" method.\textsuperscript{23,139}

Let us assume the energy $\tilde{E}$ is a function of $N$ variational parameters; $\chi_i$, $i = 1, 2, \ldots, N$, and define

$$\tilde{E} = \tilde{E}(\chi_1, \chi_2, \ldots, \chi_i, \ldots, \chi_N)$$  \hspace{1cm} (F-1)

$$\tilde{E}(i, k, m) = \tilde{E}(\chi_i^0, \chi_2^0, \ldots, \chi_i^0 + km\Delta_i, \ldots, \chi_N) \hspace{1cm} (F-2)$$

where $k = \pm 1$ and $\chi_i^0$ is an arbitrary initial value for the $i$th parameter. Here $m$ is an integer and $\Delta_i$ is a preset increment for the $i$th parameter. The variational procedures are described by the flow diagram given in Fig. (F.1).
Fig. (F-1) Flow diagram for the "Pattern Search" method used to find the minimum energies for the $H_2^+$ and $H_2$ molecules. Acc is a preset accuracy for the energy.
REFERENCES


184


   (b) E. Wigner and E.E. Witmer, Z. Physik, 51, 859 (1928).


76. J. Musher, Rev. of Mod. Phys., 39, 203 (1967).


    (b) W. Kolos and L. Wolniewicz, J. Chem. Phys.,
    (1966).
96. E.R. Davidson, Physical Chem. Vol. 3 (Academic Press,
    1969).
98. G. Herzberg, "Spectra of Diatomic Molecules"
99. G.W. King, "Spectroscopy and Molecular Structure"
100. L.D. Landau and E.M. Lifshitz, "Quantum Mechanics"
    (Pergamon Press, 1965).
102. (a) Quantum Chemistry, Program Exchange No. 88,
    (b) A.C. Wahl, P.E. Cade and C.C.J. Roothaan,
    (1959).


124. The program is based on the following papers:


130. (a) M.E. Riley, J.M. Schulman and J.I. Musher, 
      41, 986 (1964).
      38, 210 (1942).
135. J.C. Slater, "Quantum Theory of Molecules and Solids"
136. M.B. Milleur, M. Twerdochlib and J.O. Hirschfelder,
137. E. Jahnke and F. Emde, "Tables of Higher Functions"
      See also Univ. of Wisconsin Theoretical Chemistry
139. R. Hooke and T.A. Jeeves, J. Assoc. Computing Machinery,
      8, 212 (1961).