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# Generalized average local ionization energy and its representations in terms of Dyson and energy orbitals

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## Abstract

Ryabinkin and Staroverov [J. Chem. Phys. **141**, 084107 (2014)] extended the concept of average local ionization energy (ALIE) to correlated wavefunctions by defining the generalized ALIE as  $\bar{I}(\mathbf{r}) = -\sum_j \lambda_j |f_j(\mathbf{r})|^2 / \rho(\mathbf{r})$ , where  $\lambda_j$  are the eigenvalues of the generalized Fock operator and  $f_j(\mathbf{r})$  are the corresponding eigenfunctions (energy orbitals). Here we show that one can equivalently express the generalized ALIE as  $\bar{I}(\mathbf{r}) = \sum_k I_k |d_k(\mathbf{r})|^2 / \rho(\mathbf{r})$ , where  $I_k$  are single-electron removal energies and  $d_k(\mathbf{r})$  are the corresponding Dyson orbitals. The two expressions for  $\bar{I}(\mathbf{r})$  emphasize different physical interpretations of this quantity; their equivalence enables one to calculate the ALIE at any level of *ab initio* theory without generating the computationally expensive Dyson orbitals.

Keywords: ionization energy, Dyson orbitals, generalized Fock operator, reduced density matrices

## I. INTRODUCTION

The average local ionization energy (ALIE) was introduced by Politzer and co-workers<sup>1–8</sup> as an aid in interpreting the results of electronic structure calculations by the Hartree–Fock (HF) and Kohn–Sham (KS) self-consistent field (SCF) methods. It is defined<sup>9</sup> as

$$\bar{I}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \epsilon_i |\phi_i(\mathbf{r})|^2, \quad (1)$$

where  $N$  is the number of electrons in the system,  $\phi_i(\mathbf{r})$  is the spatial part of the  $i$ th occupied canonical spin-orbital,  $\epsilon_i$  is the corresponding eigenvalue, and  $\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$  is the total electron density. By Koopmans’ theorem, each  $-\epsilon_i$  provides an estimate of the ionization energy associated with the removal of an electron from the  $i$ th orbital, so  $\bar{I}(\mathbf{r})$  may be interpreted as the average energy required to remove an electron from the point  $\mathbf{r}$ . Politzer and co-workers extensively studied the ALIE and showed that it is a useful descriptor of chemical reactivity and other molecular properties.<sup>1–8</sup> We note in passing that the right-hand side of Eq. (1) may be cast in a form that is explicitly invariant under unitary transformation of the orbitals.<sup>9,10</sup>

The ALIE concept as defined by Eq. (1) or its orbital-invariant form<sup>9,10</sup> is applicable only to one-determinantal SCF methods. To overcome this limitation, Ryabinkin and Staroverov<sup>11</sup> suggested a generalization of Eq. (1) to correlated wavefunctions. They defined the generalized ALIE as

$$\bar{I}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \sum_j \lambda_j |f_j(\mathbf{r})|^2, \quad (2)$$

where  $\lambda_j$  and  $f_j(\mathbf{r})$  are, respectively, the eigenvalues and spatial parts of the eigenfunctions of the generalized Fock operator for the ground-state wavefunction of the system,  $\Psi^N$ . The eigenfunctions  $f_j(\mathbf{r})$ , called “energy orbitals”,<sup>11</sup> span the same space as the one-electron basis functions used to construct  $\Psi^N$ , and the summation in Eq. (2) extends over all such orbitals.

Although Eq. (2) correctly reduces to Eq. (1) for one-determinantal SCF methods,<sup>11</sup> it no longer has the form of a weighted average of electron removal energies. This is because the eigenvalues  $\lambda_i$  are generally *not* approximations to ionization energies. However, Eq. (2) can be rewritten in an orbital-invariant form as a sum of the local kinetic energy per electron and formal potential energy contributions,<sup>11</sup> similarly to how Eq. (1) was rewritten in Refs. 10

and 9. For this reason, Ryabinkin and Staroverov<sup>11</sup> re-interpreted the negative of the ALIE as the average local electron energy,  $\bar{\epsilon}(\mathbf{r}) = -\bar{I}(\mathbf{r})$ .

In this work, we show that the generalized ALIE of Eq. (2) can be equivalently expressed as

$$\bar{I}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_k I_k |d_k(\mathbf{r})|^2, \quad (3)$$

where  $d_k(\mathbf{r})$  are the Dyson orbitals of the system and  $I_k$  are the corresponding ionization energies. The Dyson orbitals (generalized overlap amplitudes)<sup>12–15</sup> are usually defined as

$$d_k(\mathbf{r}_1) = \sqrt{N} \sum_{\sigma_1} \int \Psi_k^{N-1*}(\mathbf{x}_2, \dots, \mathbf{x}_N) \\ \times \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (4)$$

where  $\mathbf{x}_i = \mathbf{r}_i \sigma_i$  is the collective (spatial and spin) electron coordinate and  $\Psi_k^{N-1}$  are the eigenfunctions of the  $(N-1)$ -electron Hamiltonian for the same external potential. The ionization energies here are

$$I_k = E_k^{N-1} - E^N, \quad (5)$$

where  $E^N$  and  $E_k^{N-1}$  are the total energy eigenvalues associated with  $\Psi^N$  and  $\Psi_k^{N-1}$ , respectively. The summation in Eq. (3) extends over all Dyson orbitals, that is, over all  $\Psi_k^{N-1}$ .

The equivalence of Eqs. (2) and (3) means that the generalized ALIE of Ryabinkin and Staroverov, despite its appearance, preserves and even strengthens the original interpretation of  $\bar{I}(\mathbf{r})$  as a weighted average of electron removal energies, as a proper generalization should. We will now prove and discuss this result.

## II. PROOF

Consider the ground state of a system of  $N$  electrons described by the electronic wavefunction  $\Psi^N$  which satisfies the stationary Schrödinger equation,

$$\hat{H}^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E^N \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (6)$$

where the Hamiltonian is

$$\hat{H}^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j>i}^N r_{ij}^{-1} \quad (7)$$

with

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i). \quad (8)$$

Let us partition this Hamiltonian as

$$\begin{aligned} \hat{H}^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ = \hat{h}(\mathbf{r}_1) + \sum_{j>1}^N r_{1j}^{-1} + \hat{H}^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N), \end{aligned} \quad (9)$$

where  $\hat{H}^{N-1}$  is of the same type as Eq. (7). Substitute Eq. (9) into Eq. (6), multiply the result from the left by  $N\Psi^{N*}$ , rearrange, and integrate over  $\mathbf{x}_2 \cdots \mathbf{x}_N$  to obtain

$$\begin{aligned} N\langle \Psi^N | E^N - \hat{H}^{N-1} | \Psi^N \rangle_{2\dots N} \\ = N\langle \Psi^N | \hat{h}(\mathbf{r}_1) | \Psi^N \rangle_{2\dots N} + N\langle \Psi^N | \sum_{j>1}^N r_{1j}^{-1} | \Psi^N \rangle_{2\dots N}, \end{aligned} \quad (10)$$

in obvious notation. Next we will show that the left-hand side (LHS) of Eq. (10) is equal to  $-\sum_k I_k |d_k(\mathbf{x}_1)|^2$ , while the right-hand side (RHS) is equal to  $\sum_j \lambda_j |f_j(\mathbf{x}_1)|^2$ , which will establish the equivalence of Eqs. (2) and (3).

Consider first the LHS of Eq. (10),

$$\text{LHS} = N\langle \Psi^N | E^N - \hat{H}^{N-1} | \Psi^N \rangle_{2\dots N}. \quad (11)$$

To work out this expression we invoke the expansion of  $\Psi^N$  in Dyson orbitals,<sup>16</sup>

$$\begin{aligned} \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ = \frac{1}{\sqrt{N}} \sum_k d_k(\mathbf{x}_1) \Psi_k^{N-1}(\mathbf{x}_2, \dots, \mathbf{x}_N), \end{aligned} \quad (12)$$

where  $\Psi_k^{N-1}$  are the solutions of the eigenvalue problem

$$\hat{H}^{N-1} \Psi_k^{N-1} = E_k^{N-1} \Psi_k^{N-1}. \quad (13)$$

Substituting Eq. (12) into Eq. (11) and using the orthonormality of the ionic wavefunctions,

$$\langle \Psi_l^{N-1} | \Psi_k^{N-1} \rangle = \delta_{lk}, \quad (14)$$

we obtain

$$\begin{aligned} \text{LHS} &= \sum_{kl} d_l^*(\mathbf{x}) d_k(\mathbf{x}) (E^N - E_k^{N-1}) \delta_{lk} \\ &= - \sum_k I_k |d_k(\mathbf{x})|^2, \end{aligned} \quad (15)$$

where  $I_k$  is given by Eq. (5) and the summation is over all Dyson orbitals of the system.

The RHS of Eq. (10) consists of two terms. For the first term we have

$$N\langle\Psi^N|\hat{h}(\mathbf{r}_1)|\Psi^N\rangle_{2\dots N} = \left[\hat{h}(\mathbf{r}_1)\gamma(\mathbf{x}_1, \mathbf{x}'_1)\right]_{\mathbf{x}'_1=\mathbf{x}_1}, \quad (16)$$

where

$$\begin{aligned} \gamma(\mathbf{x}_1, \mathbf{x}'_1) &= N \int \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\times \Psi^{N*}(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N \end{aligned} \quad (17)$$

is the one-electron reduced density matrix (1-RDM). The second term may be written as

$$\begin{aligned} N\langle\Psi^N|\sum_{j>1}^N r_{1j}^{-1}|\Psi^N\rangle_{2\dots N} \\ &= N(N-1) \int r_{12}^{-1} |\Psi^N|^2 d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ &= 2 \int r_{12}^{-1} \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2, \end{aligned} \quad (18)$$

where

$$\begin{aligned} \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) \\ &= \frac{N(N-1)}{2} \int \Psi^N(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \\ &\times \Psi^{N*}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) d\mathbf{x}_3 \cdots d\mathbf{x}_N \end{aligned} \quad (19)$$

is the two-electron reduced density matrix (2-RDM).

Now consider the integral operator  $\hat{G}$  with the kernel

$$G(\mathbf{x}_1, \mathbf{x}'_1) = \hat{h}(\mathbf{r}_1)\gamma(\mathbf{x}_1, \mathbf{x}'_1) + 2 \int \frac{\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \quad (20)$$

and observe that the RHS of Eq. (10) is

$$\text{RHS} = G(\mathbf{x}, \mathbf{x}). \quad (21)$$

The operator  $\hat{G}$ , known as the generalized Fock operator,<sup>17</sup> arises in various problems of electronic structure theory.<sup>18–26</sup> It is Hermitian for variational methods and non-Hermitian otherwise.<sup>17</sup> Let us symmetrize  $\hat{G}$  as

$$\hat{F} = \frac{1}{2} (\hat{G} + \hat{G}^\dagger) \quad (22)$$

and consider the Hermitian eigenvalue problem

$$\hat{F}f_j(\mathbf{x}) = \lambda_j f_j(\mathbf{x}). \quad (23)$$

Since  $\hat{F}$  is Hermitian, its eigenvalues are real and the eigenfunctions form a complete orthonormal set, so that

$$\begin{aligned} G(\mathbf{x}, \mathbf{x}) &= F(\mathbf{x}, \mathbf{x}) \equiv \langle \mathbf{x} | \hat{F} | \mathbf{x} \rangle \\ &= \sum_{ij} \langle \mathbf{x} | f_i \rangle \langle f_i | \hat{F} | f_j \rangle \langle f_j | \mathbf{x} \rangle = \sum_j \lambda_j |f_j(\mathbf{x})|^2, \end{aligned} \quad (24)$$

where the summation is over all eigenfunctions  $f_j(\mathbf{x})$ . From Eqs. (21) and (24) it follows that

$$\text{RHS} = \sum_j \lambda_j |f_j(\mathbf{x})|^2. \quad (25)$$

Comparison of Eqs. (15) and (25) gives, after eliminating the spin variable,

$$-\sum_k I_k |d_k(\mathbf{r})|^2 = \sum_j \lambda_j |f_j(\mathbf{r})|^2, \quad (26)$$

where  $d_k(\mathbf{r})$  is the spatial part of  $d_k(\mathbf{x})$  and  $f_j(\mathbf{r})$  is the spatial part of  $f_j(\mathbf{x})$ . Equation (26) implies that the representations of  $\bar{I}(\mathbf{r})$  by Eqs. (2) and (3) are equivalent. This concludes the proof for exact wavefunctions.

When the wavefunction  $\Psi^N$  is approximate, the corresponding Dyson orbitals should be understood as the overlap amplitudes between  $\Psi^N$  and wavefunctions  $\Psi_k^{N-1}$  constructed within the frozen-orbital approximation using the same correlation model as for  $\Psi^N$ . In particular, the Dyson orbitals defined in this manner for an HF SCF wavefunction  $\Psi^N$  will coincide with the canonical HF orbitals of  $\Psi^N$ . For a finite-basis-set full configuration-interaction (CI)  $\Psi^N$ ,  $\Psi_k^{N-1}$  will span the full CI space of the cationic wavefunctions constructed using the same one-electron basis set as  $\Psi^N$ . Such provisions are necessary for Eq. (26) to hold at all levels of *ab initio* theory, not just for exact wavefunctions.

It is interesting to note that the generalized ALIE naturally arises as an ingredient of various exact expressions for the exchange-correlation potential  $v_{\text{XC}}(\mathbf{r})$  of the KS density-functional theory.<sup>24–28</sup> In fact, the equivalence of Eqs. (2) and (3) is implied by the equivalence of the two exact expressions for  $v_{\text{XC}}(\mathbf{r})$  derived in Refs. 24 and 28. The above proof of this equivalence is direct. It is also noteworthy that the LHS of Eq. (26) generally contains more terms than the RHS because the number of Dyson orbitals is generally greater than the number of eigenfunctions of the generalized Fock operator.

### III. DISCUSSION

The results of Section II suggest two complementary views on the meaning of the generalized ALIE. According to Eq. (11),  $\bar{I}(\mathbf{r})$  may be defined for an arbitrary  $\Psi^N$  as

$$\bar{I}(\mathbf{r}_1) = -\frac{N}{\rho(\mathbf{r}_1)} \sum_{\sigma_1} \langle \Psi^N | E^N - \hat{H}^{N-1} | \Psi^N \rangle_{2\dots N}, \quad (27)$$

which emphasizes the connection between  $\bar{I}(\mathbf{r})$  and electron removal energies and leads to Eq. (3). Alternatively, one may write

$$\bar{I}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \left( \left[ \hat{h}(\mathbf{r}) \rho(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}} + 2 \int \frac{P(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \right), \quad (28)$$

where  $\rho(\mathbf{r}, \mathbf{r}') = \sum_{\sigma} \gamma(\mathbf{x}, \mathbf{x}')$  is the spin-free 1-RDM and

$$P(\mathbf{r}, \mathbf{r}_2) = \sum_{\sigma\sigma_2} \Gamma(\mathbf{x}, \mathbf{x}_2; \mathbf{x}, \mathbf{x}_2) \quad (29)$$

is the pair function. From Eq. (28) it follows that<sup>11</sup>

$$- \int \rho(\mathbf{r}) \bar{I}(\mathbf{r}) d\mathbf{r} = \sum_j \lambda_j = E_{\text{elec}} + V_{ee}, \quad (30)$$

where  $E_{\text{elec}}$  is the total electronic energy (without the internuclear repulsion) and  $V_{ee}$  is the (double-counted) electron-electron interaction energy. The ALIE representations by Eqs. (3) and (28) can also be related to the one-particle Green's function of the system, as implied by Ref. 29.

There is yet another instructive way of expressing the generalized ALIE. The pair function may be cast as

$$P(\mathbf{r}, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}) [\rho(\mathbf{r}_2) + \rho_{\text{XC}}(\mathbf{r}, \mathbf{r}_2)], \quad (31)$$

where  $\rho_{\text{XC}}^{\text{WF}}(\mathbf{r}, \mathbf{r}_2)$  is the exchange-correlation hole. Then Eq. (28) becomes<sup>11</sup>

$$\bar{I}(\mathbf{r}) = - \left[ \frac{\tau_L(\mathbf{r})}{\rho(\mathbf{r})} + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}^{\text{hole}}(\mathbf{r}) \right], \quad (32)$$

where

$$\tau_L(\mathbf{r}) = -\frac{1}{2} [\nabla_{\mathbf{r}}^2 \rho(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} \quad (33)$$

is the Laplacian form of the kinetic energy density,

$$v_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \quad (34)$$



is the electrostatic potential of  $\rho(\mathbf{r})$ , and

$$v_{\text{XC}}^{\text{hole}}(\mathbf{r}) = \int \frac{\rho_{\text{XC}}(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \quad (35)$$

is the exchange-correlation hole potential. The square brackets in Eq. (32) contain the sum of a local kinetic energy per electron and formal potential contributions.

Although Dyson orbitals are neither orthogonal nor normalized, nor even linearly independent, they do have the property that<sup>12</sup>

$$\rho(\mathbf{r}) = \sum_k |d_k(\mathbf{r})|^2. \quad (36)$$

By contrast, the eigenfunctions of the generalized Fock operator are orthonormal, but

$$\rho(\mathbf{r}) \neq \sum_j |f_j(\mathbf{r})|^2. \quad (37)$$

This means that the generalized ALIE is a weighted average of the ionization energies  $I_k$ , but not an average of the eigenvalues  $\lambda_i$ .

Observe that if  $\Psi^N$  is a single Slater determinant and  $\Psi_i^{N-1}$  are single determinants within the frozen-orbital (Koopmans) approximation, then the Dyson orbitals are the same as canonical spin-orbitals,  $d_i(\mathbf{x}) = \phi_i(\mathbf{x})$ , and  $I_i = -\epsilon_i$ .<sup>15</sup> For a one-determinantal  $\Psi^N$ , energy orbitals also coincide with the canonical orbitals,  $f_i(\mathbf{x}) = \phi_i(\mathbf{x})$ , and the eigenvalues of  $\hat{F}$  become  $\lambda_i = n_i \epsilon_i$ , where  $n_i = 0$  or  $1$  is the occupation number of the canonical spin-orbital  $\phi_i(\mathbf{r})$ .<sup>11</sup> This means that for HF and KS wavefunctions, Eqs. (2) and (3) both correctly reduce to Eq. (1). It is also evident that, for one-determinantal wavefunctions, Eq. (28) reduces to the ALIE expression derived by Ayers *et al.*<sup>10</sup> and by Bulat *et al.*<sup>9</sup>

Equation (30) is a generalization of the well-known result from the HF theory that the sum of the occupied HF orbital eigenvalues equals the total electronic energy with a double-counted electron interaction. The product  $\lambda_j |f_j(\mathbf{r})|^2$  may therefore be interpreted as an orbital-like contribution to the total electronic energy density with a weight  $\lambda_j$ . It is for this reason that Ryabinkin and Staroverov termed the eigenfunctions  $f_j(\mathbf{r})$  “energy orbitals”.

The original ALIE of Eq. (1) is now widely used as a tool for studying molecular properties and reactivity,<sup>1–8,30–33</sup> and in other contexts.<sup>34</sup> The generalized ALIE of Eq. (1) holds an even greater promise because it allows one to go beyond the level of one-determinantal methods and study inherently multireference systems. It is therefore of interest to discuss practical aspects of computing this quantity.

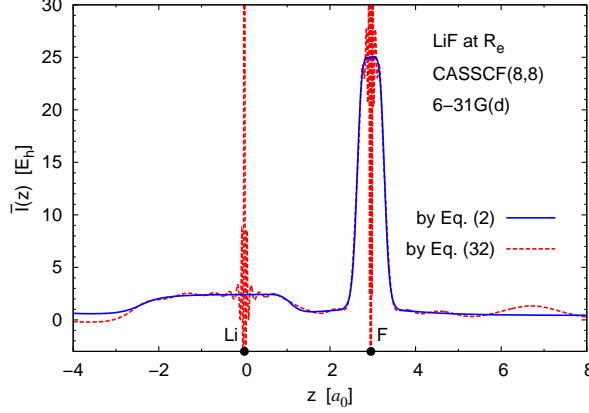


FIG. 1: Generalized ALIE computed by Eqs. (2) and (32) from a full-valence CASSCF wavefunction of the LiF molecule at  $R_e$ . The ALIE is shown along the internuclear axis.

#### IV. COMPUTING THE ALIE

We have discussed three distinct expressions for the generalized ALIE: Eqs. (2), (3), and (32). Equation (3) is impractical for computing  $\bar{I}(\mathbf{r})$  because it requires all of the Dyson orbitals and associated electron removal energies of the system (quantities that are themselves challenging to compute). Equations (2) and (32) require at most the 2-RDM, but Eq. (32) is unsuitable when Gaussian basis sets are employed, as we will now show.

Consider the HF eigenvalue problem

$$\left[ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + \hat{K} \right] \phi_i^{\text{HF}}(\mathbf{r}) = \epsilon_i^{\text{HF}} \phi_i^{\text{HF}}(\mathbf{r}), \quad (38)$$

where  $\hat{K}$  is the Fock exchange operator. If we multiply this equation by  $\phi_i^{\text{HF}*}(\mathbf{r})$ , sum over  $i$  from 1 to  $N$ , and divide by  $\rho^{\text{HF}}(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{\text{HF}}(\mathbf{r})|^2$ , we obtain<sup>9,35</sup>

$$\frac{\tau_L^{\text{HF}}(\mathbf{r})}{\rho^{\text{HF}}(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_X^{\text{hole}}(\mathbf{r}) = \frac{1}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i=1}^N \epsilon_i^{\text{HF}} |\phi_i^{\text{HF}}(\mathbf{r})|^2, \quad (39)$$

where  $v_X^{\text{hole}}(\mathbf{r})$  is the exchange-hole potential.<sup>36</sup> The RHS and LHS of Eq. (39) are equal in a complete basis set, but not when  $\phi_i^{\text{HF}}$  and other quantities are given in terms of finite-basis-set expansions. In particular, when Gaussian basis sets are used, the LHS of Eq. (39) oscillates wildly and diverges at the nuclei and at large  $r$ , whereas the RHS remains smooth and bounded.<sup>37</sup> The LHS and RHS of the inverted KS equation behave similarly.<sup>38</sup>

The eigenvalue problem for the operator  $\hat{F}$ ,

$$\int F(\mathbf{x}, \mathbf{x}') f_j(\mathbf{x}') d\mathbf{x}' = \lambda_j f_j(\mathbf{x}), \quad (40)$$

may be viewed as a generalization of the HF eigenvalue problem to post-HF wavefunctions. If we start with Eq. (40), expand the 1-RDM and 2-RDM in  $F(\mathbf{x}, \mathbf{x}')$  in terms of orthonormal energy orbitals, multiply the result by  $f_j^*(\mathbf{x})$ , sum over  $j$ , divide by  $\rho$ , and simplify, we obtain the identity<sup>24</sup>

$$\frac{\tau_L(\mathbf{r})}{\rho(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}^{\text{hole}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_j \lambda_j |f_j(\mathbf{r})|^2. \quad (41)$$

This identity expresses the equivalence of Eqs. (2) and (32) in a complete basis set. Just like Eq. (39), Eq. (41) does *not* hold when its ingredients are obtained in terms of finite-basis-set expansions. This is because the RHS of Eq. (41) contains the spectral representation of  $F(\mathbf{r}, \mathbf{r})$  which is appropriate both for complete and finite basis sets, whereas the LHS of Eq. (41) is derived by manipulations that are legitimate only in a complete basis set. Discrepancies between the LHS and RHS of Eq. (41) in finite basis sets can be dramatic: in calculations using Gaussian-type basis functions, the RHS remains well-behaved, whereas the LHS oscillates and diverges at the nuclei and at large  $r$  (Fig. 1).

Thus, when a finite basis set is employed, the ALIE should be computed either by Eq. (2) or Eq. (3), but not by Eq. (32). However, the high computational cost of Dyson orbitals makes Eq. (3) impractical and leaves Eq. (2) (together with its nondiagonal variants<sup>25,26</sup>) as the most suitable method.

## V. NUMERICAL ILLUSTRATIONS

The following illustrative calculations of the generalized ALIE were carried out using our implementation of Eq. (2) in the GAUSSIAN 09 program.<sup>39</sup> Several modules of GAUSSIAN 09 already provide matrix elements of the generalized Fock operator, so we only needed to extract the generalized Fock matrix, symmetrize it if necessary, diagonalize, and then assemble  $\bar{I}(\mathbf{r})$ .

For systems that are adequately represented by a single Slater determinant, the ALIE computed from a correlated wavefunction such as full-valence CASSCF should be similar to the ALIE computed from a HF wavefunction. This is indeed the case for a typical closed-shell molecule (LiF) at the experimental equilibrium internuclear separation,  $R_e = 2.9553a_0$  (Fig. 2). For systems with substantial multireference character, however, the HF and full-valence CASSCF ALIEs are qualitatively different—this is illustrated by Fig. 3 for a LiF molecule stretched to  $3R_e$ . The key difference between the HF and CASSCF ALIEs for

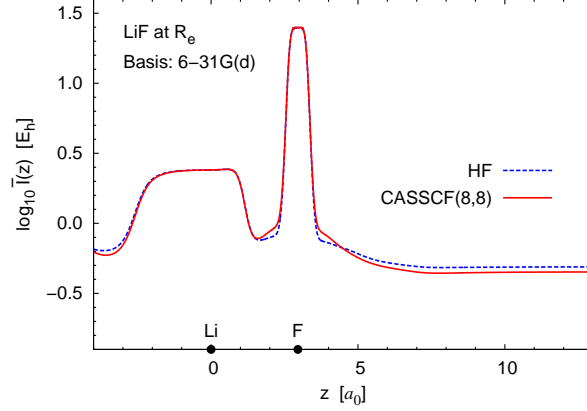


FIG. 2: ALIEs for the LiF molecule at  $R_e$  computed from HF and full-valence CASSCF wavefunctions and shown along the internuclear axis. Note the logarithmic scale for  $\bar{I}(z)$ . The two curves are similar.

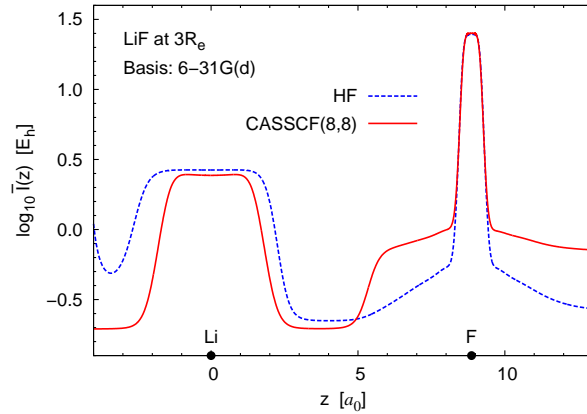


FIG. 3: ALIEs for a stretched LiF molecule ( $3R_e$ ) computed from HF and full-valence CASSCF wavefunctions and shown along the internuclear axis. Note the logarithmic scale for  $\bar{I}(z)$ . The CASSCF ALIE has a step near  $z = 5a_0$ .

a stretched LiF is the upshift of the correlated ALIE around the more electronegative F atom and the resulting step of  $\bar{I}(\mathbf{r})$ . Similar upshifts appear in exact exchange-correlation potentials of all stretched heteronuclear diatomics and are responsible for the dissociation of such molecules into neutral atoms rather than pairs of ions.<sup>40–45</sup> In fact, ALIEs generated from accurate correlated wavefunctions encapsulate the complete information about the height and position of the steps in molecular exact exchange-correlation potentials.<sup>45</sup>

At  $3R_e$ , the CASSCF ALIE in LiF assumes values of about  $0.2 E_h$  around the Li atom and  $0.6$ – $0.7 E_h$  around the F atom (Fig. 3). These values are consistent with the corresponding

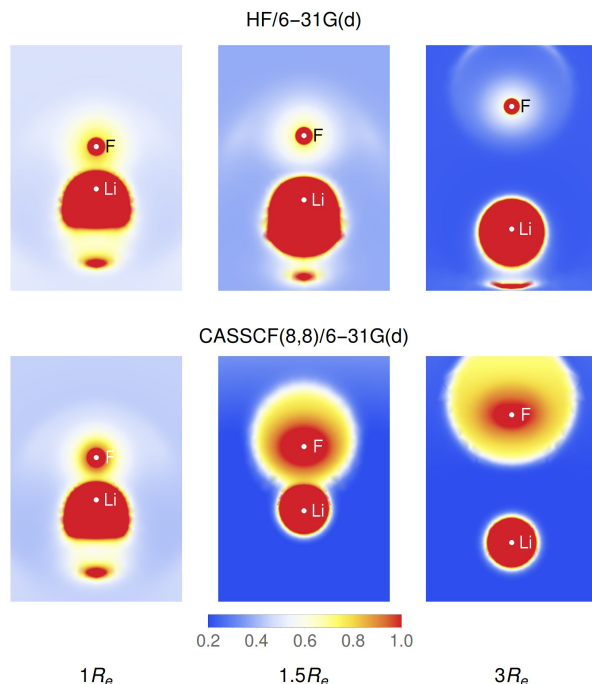


FIG. 4: Color maps of the ALIEs from the HF and full-valence CASSCF wavefunctions of the LiF molecule computed at the equilibrium distance ( $R_e$ ), for a moderately stretched bond ( $1.5R_e$ ), and for a nearly dissociated molecule ( $3R_e$ ).

exact first ionization energies of the isolated Li and F atoms:  $I_{\text{Li}} = 0.198 E_h$  and  $I_{\text{F}} = 0.641 E_h$ ,<sup>46</sup> as should be the case for an accurate generalized ALIE.<sup>11,45</sup> The HF ALIE does not behave this way because it has neither correct asymptotic values nor the step structure (Fig. 3).

Figure 4 conveys the same message as Figs. 2 and 3 in the form of ALIE color maps in the plane containing the internuclear axis of the LiF molecule. For  $R = R_e$ , the HF and full-valence CASSCF ALIEs are similar but become distinct with increasing  $R$ . In the CASSCF ALIE map for  $R = 3R_e$ ,  $\bar{I}$  asymptotically approaches  $I_{\text{Li}} \approx 0.2 E_h$  in all directions. This is because the generalized ALIE has the property<sup>11</sup>  $\lim_{r \rightarrow \infty} \bar{I}(\mathbf{r}) = I$ , where  $I$  is the first ionization energy of the system, and because the ionization energy of a highly stretched heteronuclear diatomic is equal to the ionization energy of its less electronegative atom.

Another instructive way to represent the ALIE is to construct a molecular isodensity surface, typically for a density value defining the van der Waals surface of the molecule (e.g.,  $0.001 e/a_0^3$ ), and then “paint” that surface with colors according to the magnitude of the ALIE. This method has been extensively used by the Politzer group for studying chemical

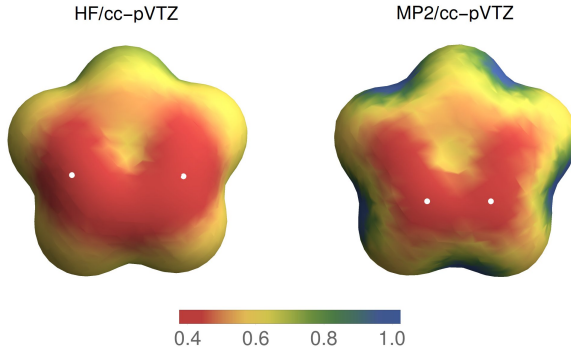


FIG. 5: HF and MP2 ALIEs on the  $0.001 e/a_0^3$  isodensity surfaces of the pyrrole molecule ( $C_4H_5N$ ). The N atom (atom 1) is at the top. Each density is generated from the same wavefunction as the corresponding ALIE. The white dots marks the points with the lowest ALIE values on the surface.

reactivity in terms of the HF and KS ALIEs.<sup>1–8</sup> Such rendering can be particularly effective for comparing the ALIEs derived from one-determinantal and correlated wavefunctions. Consider, for instance, the heterocyclic pyrrole molecule ( $C_4H_5N$ ) whose five atoms forming the ring are labeled 1 through 5 starting with the nitrogen. On the van der Waals surface of this molecule, the HF ALIE attains the smallest values roughly halfway between atoms 2 and 3 (and in the equivalent position between atoms 4 and 5), whereas the ALIE computed by the second-order Møller–Plesset (MP2) perturbation theory has the smallest value near atoms 3 and 4 (Fig. 5). One can say that, according to the MP2 ALIE map, it is easier to remove an electron from atoms 3 and 4 than from atoms 2 and 5, whereas the HF ALIE prediction does not reveal a clear preference. Experiments show that electrophilic attack on pyrrole *in the gas phase* indeed occurs predominantly at atoms 3 and 4 ( $\beta$  position).<sup>47–49</sup> Examples like this demonstrate that a correlated ALIE can give qualitatively correct reactivity predictions where the HF ALIE would be at odds with experiment.

## VI. CONCLUSION

We have demonstrated that the generalized ALIE,  $\bar{I}(\mathbf{r})$ , can be represented in a complete (infinite) basis set by any of the following three simple expressions: Eqs. (2), (3), or (32). Equation (3) preserves the meaning of  $\bar{I}(\mathbf{r})$  as a weighted average of ionization energies, while Eqs. (2) and (32) suggest a re-interpretation of  $-\bar{I}(\mathbf{r})$  as an average local electron energy. Equation (3) provides a clearer physical interpretation of the ALIE than Eq. (2),

while the latter is more convenient for practical calculations of  $\bar{I}(\mathbf{r})$  because Dyson orbitals are less accessible than the generalized Fock matrix.

Ref. 11 assumed that Eqs. (2) and (32) could be used interchangeably for computing the ALIE. In this work, we showed that Eq. (32) is unsuitable for computing  $\bar{I}(\mathbf{r})$  when the parent 2-RDM is given in terms of Gaussian basis functions. Thus, Eq. (2) is the only viable general method for calculating the ALIE.

The equivalence of Eqs. (2) and (3) proved in this work is significant because it allows one to compute the generalized ALIE, a molecular descriptor related to *all* first ionization energies and Dyson orbitals of the system, without generating those energies and orbitals themselves. It opens up practically unlimited possibilities for exploring molecular properties through the ALIE concept at any level of *ab initio* theory beyond the HF and approximate density-functional techniques.

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