Average Local Ionization Energies in the Hartree−Fock and Kohn−Sham Theories

Felipe A. Bulat,*[†] Mel Levy,*[†,‡] and Peter Politzer*[§,||]

Department of Chemistry, Duke University, Durham, North Carolina 27708, Department of Chemistry, Tulane University, New Orleans, Louisiana 78118, Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

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We explore the connection between average local ionization energies computed within the Hartree−Fock (HF) and the Kohn−Sham (KS) frameworks, focusing on exchange-only KS theory. We find that they are connected through a local quantity for which good approximations exist; $\bar{I}_{HF}(r) = \bar{I}_{KS}(r) + \Delta V_X(r)$. This allows determination of HF local ionization energies from exchange-only KS calculations without utilizing a nonlocal potential. We also suggest interesting research directions that emerge during our analysis.

Introduction

The ionization energy (I) is one of the most fundamental properties of atomic and molecular systems. It is defined as the energy necessary to remove one electron, or to "ionize" a system

$$I = E[N-1] - E[N] \qquad (1)$$

As such, I measures the ease (or lack thereof) with which a system can let go of one of its electrons. It is related via finite difference approximation procedures to the electronic chemical potential and hardness of density functional theory (DFT).[1] One of the great successes of DFT has been in providing mathematical foundations for established chemical concepts. The chemical potential and the hardness govern the distributions of electrons within molecules and in their interactions. For interpreting and predicting molecular reactivity, however, "global" quantities are not very useful, since reactivity is site specific. Thus, rather than just the global ionization energy, which tells how likely is a molecule to share its electronic charge, it is also important to know from where in the molecule is this charge most likely to come. A great number of "local" quantities are routinely used to describe molecular reactivity, including reactivity indices afforded by DFT. Among these, the Fukui functions[2−4] stand out, because they predict the most likely reactive sites for the addition and removal of charge, as well as for radical processes. There is also the so-called "dual descriptor",[5] closely related to the Fukui functions and capable of predicting preferred sites for both addition and removal of charge through only one "local" quantity.

We shall be interested in a local version of the ionization energy, introduced by Sjoberg et al.[6] in the context of Hartree−Fock (HF) theory. The average local ionization energy $\bar{I}(r)$ is defined as

$$\bar{I}(r) = -\frac{\sum_i^{occ} \varepsilon_i \rho_i(r)}{\rho(r)} \qquad (2)$$

where ε_i and $\rho_i(r)$ are the HF eigenvalues and orbital densities, respectively. $\bar{I}(r)$ is a measure of how tightly bound electrons are at a given point in space r, an interpretation afforded by Koopmans' theorem[7] that (approximately) relates HF orbital energies to the ionization energies. The focus is thus upon a particular point in space, with contributions from all the orbitals rather than on a particular orbital. Although Koopmans' theorem certainly played a motivational role in developing eq 2[6] as well as the basis for its interpretation, $\bar{I}(r)$ is perhaps best justified by its widespread use and effectiveness, having found very diverse applications in the realm of chemical reactivity in particular, and chemical theory in general.[8]

One notable feature of $\bar{I}(r)$ is that it reproduces atomic shell structure. If one takes the inflection points in $\bar{I}(r)$ as the boundaries between shells, the integrated shell populations correspond well with the formal ones.[9] It is very satisfying that the average local ionization energy is relatively constant within each atomic shell, with significant jumps between shells; this corresponds well with chemical intuition.

When computed over a molecular surface (defined as, say, the $\rho(r) \equiv 0.001$ au isodensity surface following Bader et al.),[10] $\bar{I}(r)$ then provides a way of computing the valence electrons' local ionization energy without the need to actually identify the valence regions explicitly.[11] Thus, it relates in a very straightforward manner to Allen's electronegativity.[12−14]

The average local ionization energy $\bar{I}(r)$ has also proved reliable in describing molecular reactivity toward electrophiles, which is usually done by examining $\bar{I}(r)$ on molecular surfaces and subsequently identifying the regions of its minimum values. These regions indicate the least tightly bound, most reactive electrons. The positions of $\bar{I}(r)$ minima have been observed to correlate well with, for example, preferred sites in electrophilic aromatic substitutions.[6] They are also a valuable tool in the characterization of aromaticity and radical sites.[15] $\bar{I}(r)$ has been found to correlate well with diverse quantities such as polarizability, hardness, and Hammett constants.[8] It should be noted that $\bar{I}(r)$ has been linked to the Fukui function governing interactions with electrophiles.[16]

Because of the widespread use of $\bar{I}(r)$, we aim in the present article to explore the formal differences between its HF ($\bar{I}_{HF}(r)$) and Kohn−Sham (KS) versions ($\bar{I}_{KS}(r)$), with an emphasis on exchange-only KS formalism. We show that there exists an approximate relationship between $\bar{I}_{HF}(r)$ and $\bar{I}_{KS}(r)$ and that one can be computed from the other. It is remarkable that these are (approximately) connected by a purely local quantity, for which

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* To whom correspondence should be addressed. E-mail: felipe.bulat@duke.edu (F.A.B.); mlevy@tulane.edu (M.L.); ppolitze@uno.edu (P.P.).

[†] Duke University.

[‡] Tulane University.

[§] University of New Orleans.

[||] Cleveland State University.

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TABLE 1: HF and KS Eigenvalues for the Occupied Orbitals of Ne, Ar, N_2, and CO[a]

Neon		Argon	
HF	KS	HF	KS
−32.7654	−30.9529 (1.8125)	−118.6110	−114.8037 (3.8074)
−1.9190	−1.4805 (0.4385)	−12.3188	−11.4749 (0.8439)
−0.8323	−0.6123 (0.2200)	−9.5684	−8.9839 (0.5845)
−0.8323	−0.6123 (0.2200)	−9.5684	−8.9839 (0.5845)
−0.8323	−0.6123 (0.2200)	−9.5684	−8.9839 (0.5845)
		−1.2743	−1.0665 (0.2078)
		−0.5880	−0.5544 (0.0336)
		−0.5880	−0.5544 (0.0336)
		−0.5880	−0.5544 (0.0336)
N_2		CO	
−15.6777	−14.1628 (1.5150)	−20.6706	−19.1014 (1.5692)
−15.6736	−14.1611 (1.5125)	−11.3571	−10.2632 (1.0939)
−1.4951	−0.9907 (0.5044)	−1.5407	−1.2195 (0.3212)
−0.7642	−0.3871 (0.3771)	−0.8047	−0.6257 (0.1790)
−0.6294	−0.3262 (0.3032)	−0.6457	−0.5312 (0.1145)
−0.6224	−0.3262 (0.2962)	−0.6457	−0.5312 (0.1145)
−0.6224	−0.2821 (0.3403)	−0.5458	−0.4074 (0.1384)

[a] The values in parentheses are the differences between the HF and KS results ($\varepsilon_i^{KS} - \varepsilon_i^{HF}$).

good approximations exist. $\bar{I}_{HF}(r)$ can thus be determined from $\bar{I}_{KS}(r)$, which implies some knowledge of the HF eigenspectra without evaluating any nonlocal operator. During our analysis, we also sketch several research directions related to $\bar{I}(r)$ that should both shed light on its intriguing features and also play an important role in its further development and applications.

Theory. In the following, we make use of the HF and KS equations to understand the relationship between the average local ionization energies and other quantities of interest, such as the kinetic energy density, local temperature, electrostatic potential, etc. Many of these relationships have been stated before, but they represent a good starting point for understanding $\bar{I}(r)$ and constitute a fundamental step in unveiling a (local) connection between the HF and the exchange-only KS eigenspectra.

The one-particle HF equations are

$$\left\{-\frac{1}{2}\nabla^2 + \hat{\upsilon}_{HF}(r)\right\}\psi_i(r) = \varepsilon_i\psi_i(r) \qquad (3)$$

where ε_i and $\psi_i(r)$ are the canonical HF eigenvalues and eigenvectors, respectively, and

$$\hat{\upsilon}_{HF}(r)\psi i(r) = \{\upsilon_{ext}(r) + \upsilon J(r)\}\psi i(r) + \sum_a^{occ}\int \psi a(r')(r-r')^{-1}\psi i(r')\mathrm{d}r'\,\psi a(r) \qquad (4)$$

$\upsilon_{ext}(r)$ is the potential due to the nuclei, and $\upsilon_J(r)$ the classical Coulomb potential due to the electronic charge distribution. Left multiplying in eq 3 by $\psi_i^*(r)$, we have

$$-\frac{1}{2}\psi_i^*(r)\nabla^2\psi_i(r) + \psi_i^*(r)\hat{\upsilon}_{HF}(r)\psi_i(r) = \varepsilon_i\psi_i^*(r)\psi_i(r) = \varepsilon_i\rho_i(r) \qquad (5)$$

where $\rho_i(r) = \psi_i^*(r)\psi_i(r)$ is the orbital density. We stress the fact that the product $\varepsilon_i\rho_i(r)$ is the single-particle energy density for the ith orbital, a very simple yet not widely appreciated result. This justifies taking the sum of all orbital energy densities in eq 2 to obtain the total, independent-particle energy density in the numerator, which can also be regarded as the total independent-particle ionization energy density.

We now sum over all the occupied orbitals in eq 5 to obtain the numerator of eq 2 on the right-hand side

$$-\frac{1}{2}\sum_i^{occ}\psi_i^*(r)\nabla^2\psi_i(r) + \upsilon_{ESP}(r)\sum_i^{occ}\rho_i(r) + \sum_i^{occ}\psi_i^*(r)\hat{\upsilon}_{HF}^{nl}(r)\psi_i(r) = \sum_i^{occ}\varepsilon_i\rho_i(r) \qquad (6)$$

where we have split the HF operator $\hat{\upsilon}_{HF}(r)$ into its local ($\upsilon_{ESP}(r)$) and a nonlocal ($\hat{\upsilon}_{HF}^{nl}(r)$) contributions. The local part is simply the electrostatic potential $\upsilon_{ESP}(r)$ at r (sum of the external $\upsilon_{ext}(r)$ and Coulomb $\upsilon_J(r)$ potentials), whereas the nonlocal part $\hat{\upsilon}_{HF}^{nl}(r)$ involves the more complicated orbital-dependent expression in eq 4. The third term in eq 6 is readily seen to correspond to the Slater potential times the total density

$$\sum_i^{occ}\psi_i^*(r)\hat{\upsilon}_{HF}^{nl}(r)\psi_i(r) = \upsilon_{Slater}(r)\rho(r) \qquad (7)$$

It then follows from eq 6 that

$$\frac{t_s(r)}{\rho(r)} + \upsilon_{ESP}(r) + \upsilon_{Slater}(r) = \frac{\sum_i^{occ}\varepsilon_i\rho_i(r)}{\rho(r)} \qquad (8)$$

where $t_s(r)$ is the local kinetic energy density, herein defined as $t_s(r) = -{}^1/_2\Sigma_i^{occ}\psi_i^*(r)\nabla^2\psi_i(r)$. Eq 8 reveals an interesting connection,

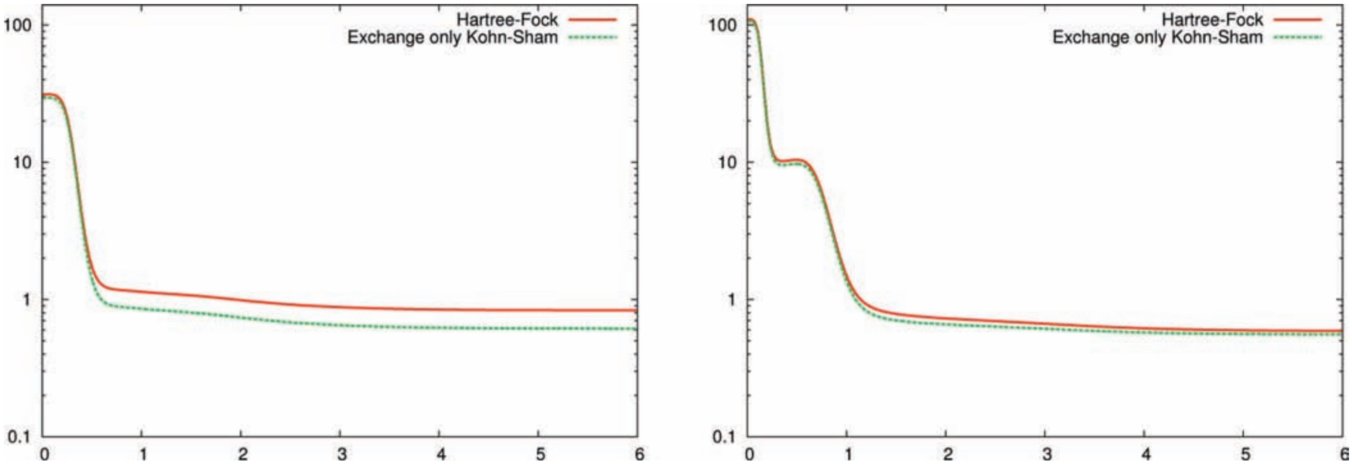

Figure 1. $\bar{I}_{HF}(r)$ and $\bar{I}_{KS}(r)$ for neon (upper panel) and argon (lower panel).

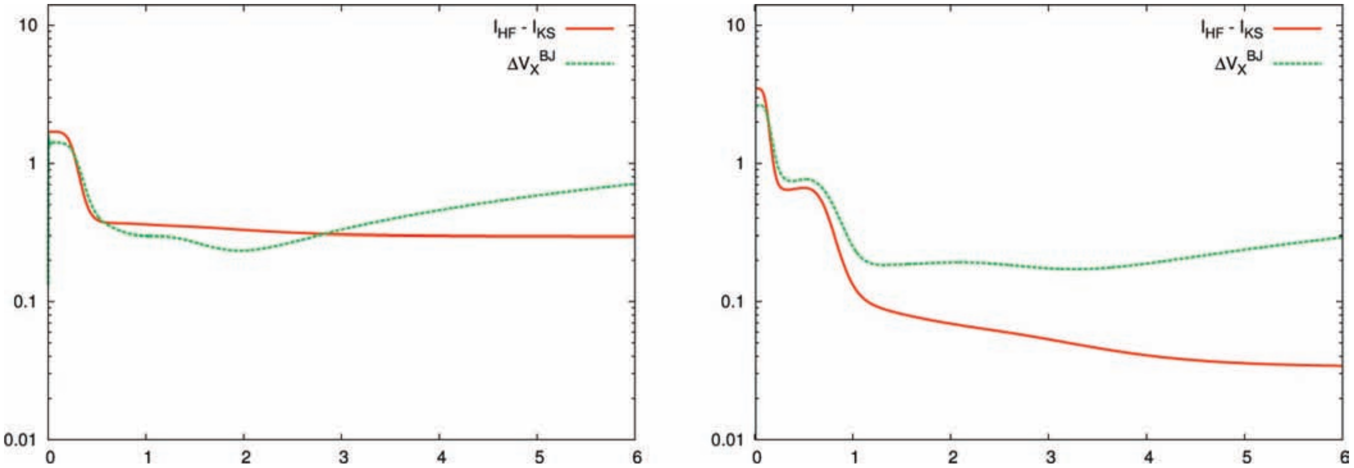

Figure 2. $\Delta V_X(r) = \bar{I}_{\mathrm{HF}}(r) - \bar{I}_{\mathrm{KS}}(r)$ for neon (upper panel) and argon (lower panel). Also shown is the BJ approximation to $\Delta V_X(r)$.

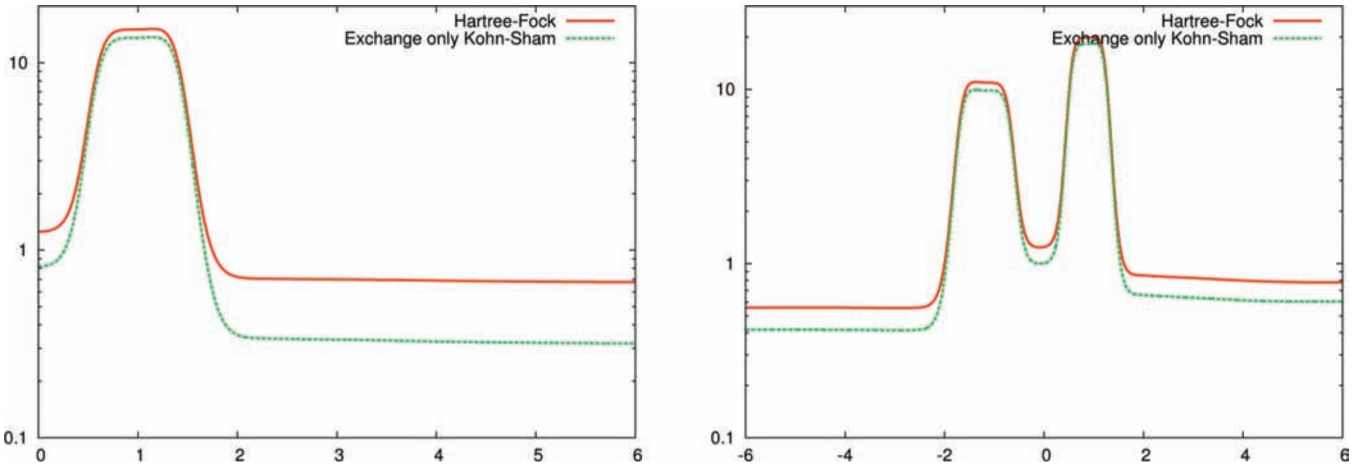

Figure 3. $\bar{I}_{\mathrm{HF}}(r)$ and $\bar{I}_{\mathrm{KS}}(r)$ for molecular nitrogen (upper panel) and carbon monoxide (lower panel) along the C_∞ axes. The nitrogen atoms are at located at ±1.01 au, and only half of the axis is shown. The carbon and oxygen atoms are located at -1.19 and 0.89 au, respectively.

via the Slater potential, between three widely used reactivity descriptors, the local electronic temperature $T(r)$, the electrostatic potential $V_{\mathrm{ESP}}(r)$, and the average local ionization energy $\bar{I}(r)$

$$\frac{3}{2}kT(r) + v_{\mathrm{ESP}}(r) + v_{\mathrm{Slater}}(r) = -\bar{I}_{\mathrm{HF}}(r) \qquad (9)$$

where k is the Boltzmann constant. Eq 8 is also interesting because it reveals that, contrary to what might be expected based on its definition through HF canonical eigenvalues and eigenvectors, $\bar{I}(r)$ is invariant to unitary transformations. This can be seen by examining the left-hand side of eq 8 term by term. This is indeed very interesting, because it indicates that eq 8 (or eq 9) is perhaps a more general definition of $\bar{I}(r)$. We will come back to this shortly.

In eq 9 above, we introduce the notation $\bar{I}_{\mathrm{HF}}(r)$ to emphasize that this represents the average local ionization energy computed with HF eigenvalues and eigenvectors. Below, we will introduce the analogous quantity $\bar{I}_{\mathrm{KS}}(r)$, which is computed with KS eigenvalues and eigenvectors. It will be of significant interest to compare these two quantities.

An analogous derivation to that given above in detail for HF yields an expression for the KS equivalent to eq 9, the difference being that the Slater potential is replaced by the exchange-correlation potential $v_{\mathrm{XC}}(r)$

$$\frac{3}{2}kT(r) + v_{\mathrm{ESP}}(r) + v_{\mathrm{XC}}(r) = -\bar{I}_{\mathrm{KS}}(r) \qquad (10)$$

Note that eq 9 utilizes the HF determinant, while eq 10 utilizes the KS determinant. It then follows that $T(r)$ and $v_{\mathrm{esp}}(r)$ in eqs 9 and 10 are generally different. We use the same symbol because in further exploring the relationship between the HF and KS schemes, we will assume that the HF and KS determinants are identical (vide supra).

One needs to keep in mind that buried in eqs 9 and 10 are the HF and KS eigenvalues and eigenvectors, respectively. Ayers et al.[17] arrived at a slightly different but equivalent version of eq 10 (eq 60 in ref 17 in which a different definition of the kinetic energy density and hence of the local temperature was used), while Ghosh et al.[18] came very close even before the average local ionization energy eq 2 was introduced. Indeed, by use of the Euler equation in eq 26 of ref 18, one arrives at an analogous relationship. Ghosh and Balbas[19] also analyzed similar relationships (see eq 5 in ref 19) in the context of the HF kinetic energy density functional.

An interesting consequence of eqs 9 and 10 is that, as mentioned above, they offer an alternative definition of the average local ionization energy, namely

$$\bar{I}_{\mathrm{KS}}[\rho(r), r] = -\frac{t_s[\rho(r), r]}{\rho(r)} - v_{\mathrm{ESP}}[\rho(r), r] - v_{\mathrm{XC}}[\rho(r), r] \qquad (11)$$

$\bar{I}(r)$ is defined by eq 11 as a functional of the electronic density, and no explicit reference to the orbitals and eigenvalues is required. Indeed, each of the terms in eq 11 is a functional of the density. While computing each of these terms accurately usually requires orbitals; they are, in principle, not needed. Furthermore, since $\bar{I}(r)$ is usually of most interest on isodensity

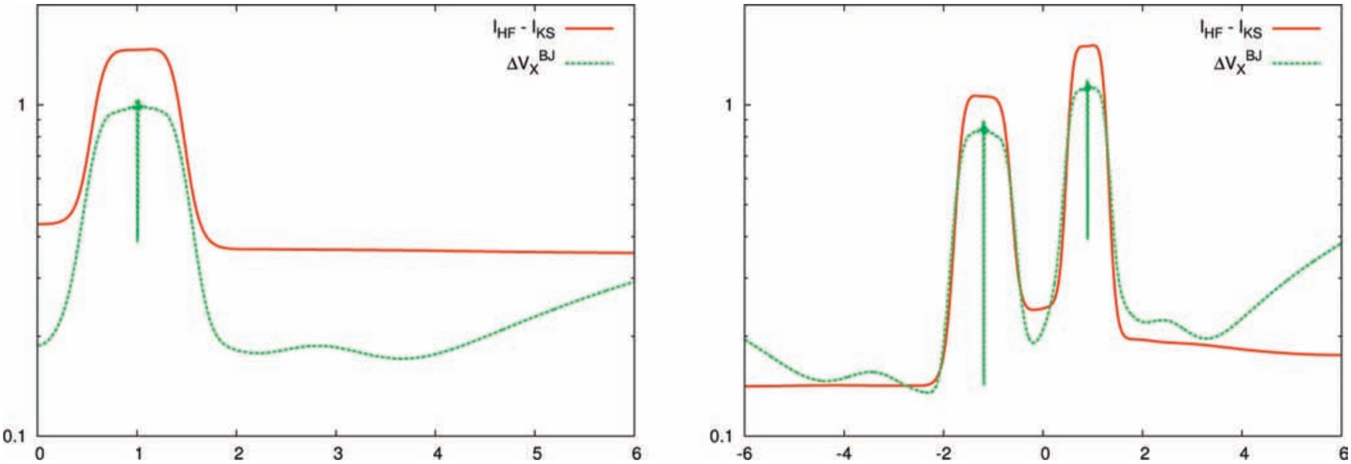

Figure 4. $\Delta V_X(r) = \bar{I}_{HF}(r) - \bar{I}_{KS}(r)$ for molecular nitrogen (upper panel) and carbon monoxide (lower panel) along the C_∞ axes. Also shown is the BJ approximation for $\Delta V_X(r)$.The nitrogen atoms are at located at ±1.01 au, and only half of the axis is shown. The carbon and oxygen atoms are located at −1.19 and 0.89 au, respectively.

molecular surfaces, which are much like a homogeneous electron gas, it may turn out that currently available kinetic energy density functionals approximate $t_s[\rho(r)]$ well such a surface. Density-based reactivity descriptors are rare, because one usually resorts to orbitals. Eq 11 thus provides the opportunity of filling this gap. This could be of particular interest in the study of the reactivities of large systems, in the context of orbital-free density functional theory. $\bar{I}(r)$ is actually very appropriate for large systems. Because of their normalization constraints, indices such as the Fukui functions tend to have very small values everywhere for orbitals delocalized over large regions of space. This does not mean that the reactivity is equal everywhere but rather that the small values afforded by the Fukui functions in such situations make them hard to interpret. In contrast, because $\bar{I}(r)$ constitutes an energy density, it is equally reliable for small and large systems. An additional advantage of $\bar{I}(r)$ is that it can be compared for molecules regardless of size, type, electron localization/delocalization, etc., whereas Fukui functions are very hard to compare among different molecules (especially of varying sizes), and one has to resort to other indices such as local hardnesses, which are in general more difficult to compute reliably. Interestingly, $\bar{I}(r)$ also appears to be related to local hardness.[20]

Mention of the normalization of reactivity indices raises the question of whether $\bar{I}(r)$ obeys any such constraint. It is easily seen from its definition, eq 2, that $\bar{I}(r)$ tends to the highest occupied orbital (hoo) energy ε_{hoo} as r tends to infinity

$$\lim_{r\to\infty} \frac{\sum_i \varepsilon_i \rho_i(r)}{\rho(r)} = \lim_{r\to\infty} \frac{\varepsilon_{\text{hoo}}\rho_{\text{hoo}}(r)}{\rho_{\text{hoo}}(r)} = \varepsilon_{\text{hoo}} \tag{12}$$

because at large r both the total density $\rho(r)$ and the total independent-particle energy density $\Sigma_i^{\text{occ}}\varepsilon_i\rho_i(r)$ are dominated by $\rho_{\text{hoo}}(r)$. Although $\bar{I}(r)$ is normalized in the sense of eq 12, the integral of $\bar{I}(r)$ over all space will thus diverge, and we see that $\bar{I}(r)$ obeys no normalization condition in this sense (analogous to the normalization of the Fukui functions, whose integrals over all space are bound and yield unity). The situation could arguably be remedied by taking the integral of $\bar{I}(r)-\varepsilon_{hoo}$, or by integrating $\bar{I}(r)$ only within the subspace defined by the molecular surface. This is far from the objectives of the present study, and it is suggested as an interesting research direction.

Another interesting feature of eq 11 is that it decomposes the average local ionization energies into three different contributions. Because $\bar{I}(r)$ has proven to be such a valuable tool, it is interesting to understand which of these three contributions determines its features, particularly on molecular surfaces and at its minima on these surfaces, which are the sites of the most reactive electrons.

In the following we shall be mainly interested in exchange-only KS. We rewrite the exact $v_X(r)$ as the Slater potential plus a correction

$$v_X(r) = v_{\text{Slater}}(r) + \Delta V_X(r) \tag{13}$$

and note that $\Delta V_X(r)$ has been studied (and approximated) by several authors.[21−27] Eq 10 then becomes

$$\frac{3}{2}kT(r) + v_{\text{ESP}}(r) + v_{\text{Slater}}(r) + \Delta V_X(r) = -\bar{I}_{KS}(r) \tag{14}$$

As stated earlier, the exchange-only KS and the HF density matrices are usually very similar to each other,[28] so that $\rho(r)$, $t_s(r)$ (and thus $T(r)$), and $v_{\text{Slater}}(r)$ computed from the either set of eigenvectors should also be very close to each other. The point to note here is that it is not required that the canonical HF orbitals be like the KS for the first three terms in eqs 14 and 9 to be close to each other. All that is required is that the determinants be similar. Because of the connection between the ground-state HF and KS determinants demonstrated by Ivanov and Levy,[28] we expect this to be the case. With this in mind, compare eqs 9 and 14 to arrive at the conclusion that the HF and KS local ionization energies are approximately related to each other through

$$\bar{I}_{HF}(r) = \bar{I}_{KS}(r) + \Delta V_X(r) \tag{15}$$

Eq 15 remarkably allows the computation of $\bar{I}_{HF}(r)$ from DFT calculations (or vice versa) without resorting to the evaluation of any nonlocal quantity. Conceptually, this brings to mind the fact that the interelectronic repulsion energy in atoms and molecules can be related rigorously to the electrostatic potentials at nuclei.[29,30] The equality in eq 15 only holds exactly if the HF and KS density matrices are identical, in which case the local temperature $T(\mathbf{r})$, electrostatic potential $v_{\text{ESP}}(\mathbf{r})$, and Slater v_{Slater} $(\mathbf{r})$ potentials in eqs 9 and 14 cancel exactly. However we will provide evidence of the accuracy of eq 15, which rests on the close connection between the KS and the HF determinants.[28]

We now further explore the Becke−Johnson (BJ) approximation for $\Delta V_X(r)$

$$\Delta V_X^{BJ}(r) = C_X \sqrt{\frac{\tau(r)}{\rho(\mathrm{r})}} \tag{16}$$

where $C_X = (1/\pi)\sqrt{5/12}$ and $\tau(r) = \Sigma_i^{occ}|\nabla\psi_i(r)|^2$ as an approximate way of going from $\bar{I}_{KS}(r)$ to $\bar{I}_{HF}(r)$. It is interesting to note that $\Delta V_X^{BJ}(r)$ is always positive, consistent with the general observation[8,15,31] that $\bar{I}_{KS}(r) < \bar{I}_{HF}(r)$. This result can be generalized by noting that the Slater potential is conjectured to be a lower bound to the full exchange potential in KS theory. We would like to mention that, in our implementation, $\Delta V_X^{BJ}(r)$ is computed in a Gaussian basis, and thus it diverges it long-range (whereas strictly speaking is should asymptotically approach a constant whose value depends on ε_{hoo}),[26] and it is not well behaved at or very close to the nuclear positions.

Results

To test the validity of eq 15, we have performed calculations on a small set of atoms (neon and argon) and molecules (molecular nitrogen and carbon monoxide). The HF and (exchange-only) KS wave functions were obtained using double-ζ basis sets (cc-pVDZ). For the KS calculations, the optimized effective potential (OEP) method was used as implemented by Wu and Yang.[32] We employ the following construction for the potential in our OEP calculations

$$v_s(r) = v_{ext}(r) + v_0(r) + \sum_t b_t g_t(r) \tag{17}$$

where $v_{ext}(r)$ is the external potential due to the nuclei, $v_0(r)$ is a reference potential, and $\Sigma_t b_t g_t(r)$ is a sum of Gaussian basis functions $g_t(r)$ with expansion coefficients b_t. We chose to use the Fermi−Amaldi potential[33] as $v_0(r)$ in eq 17, because it ensures that the total KS potential $v_s(r)$ has the correct long-range behavior, which is important for determining ε_{hoo}. However, we note that for our present purposes it is quite irrelevant whether the KS potential tends to zero or to any arbitrary constant, because it can be seen in eq 15 that an arbitrary constant in the potential will enter both terms on the right-hand side with opposite signs, so that they will cancel. Of course, the potential still needs to decay as $1/r+C$, but it makes no difference whether C equals zero or any other real number.

To ensure that the KS eigenvalues and eigenvectors do not collapse to the HF (Staroverov et al.[34] show that this can happen) and that they come from a local, multiplicative potential, we use the L curve approach developed by Heaton-Burgess, Bulat, and Yang.[35] By using large potential basis sets coupled to the L curve approach, the results become independent of the potential basis, further ensuring that a physically meaningful exchange potential is obtained. By "physically meaningful" we mean that the potential is consistent with the true functional derivative of the energy formula, which means it does not display large oscillations. The true v_X obeys the virial relation[36] and more generally obeys all three Ou-Yang and Levy conditions.[37,38] We choose the corner of the L curve or the maximum in the reciprocal slope[39] as the criteria for the optimal potential, because both have been seen to produce reliable results[35,39,40] and are invariably very close to each other.

Table 1 collects the HF and the KS eigenvalues, along with their differences, for the atomic and molecular systems considered. The most interesting observation is, perhaps that the HF eigenvalues are always larger in magnitude and that the differences are not constant. This had indeed been pointed out by Abu-Awwad and Politzer,[31] but they did not consider the case of HF versus exact-exchange only KS, for which the energy functional is the same and the difference comes entirely from the restriction that the KS potential needs to be local and multiplicative. The other interesting observation is the rather large difference for the hoo of N_2, but this will not be of much concern here (vide infra), partly because a constant in the potential does not change anything in our analysis, as explained above.

Figure 1 shows the local ionization energies of neon and of argon as functions of the radial distances from the nuclei. It is immediately apparent that the shell structure is revealed and that the different shells can be identified with the regions in which $\bar{I}(r)$ is approximately constant. It is also seen that the KS and HF results appear, at least on this scale, to be quite similar, although their difference is clearly not constant. Figure 2 presents the difference $\Delta V_X(r)$ between the HF and KS results, which is seen to be very similar in overall shape to $\bar{I}(r)$ itself. Figure 2 also shows the BJ approximation $\Delta V_X^{BJ}(r)$, which is seen to be a fairly good approximation to $\Delta V_X(r)$. It should be emphasized that these results are not entirely fair to the BJ approximation, because $\Delta V_X^{BJ}(r)$ was computed in a Gaussian basis and, as mentioned before, can diverge in such a basis. It would be interesting to revisit these results using Slater functions or a numerical code, and we would expect that $\Delta V_X^{BJ}(r)$ would perform even better. Another interesting observation is that $\Delta V_X^{BJ}(r)$ computed with the HF orbitals (in the kinetic energy density expression) and density is almost indistinguishable from that obtained using the KS orbitals. At the scale of the plots in Figure 2, they lie on top of each other, so only one is plotted.

These observations are significant because they constitute important evidence that the first three terms in eq 9 are very close to the first three terms in eq 14. This suggested that perhaps it makes difference in the HF and KS eigenvalues and not in their determinants. This means that it makes little difference whether the KS eigenvalues are combined with the KS or HF orbitals in computing $\bar{I}_{KS}(r)$ or whether the HF eigenvalues are combined with the HF or KS orbitals in computing $\bar{I}_{HF}(r)$. This is indeed seen to be the case (data not shown), and the quantity

$$-\frac{\sum_i^{occ} \varepsilon_i^{KS} \rho_i^{HF}(r)}{\rho^{HF}(r)} - \left(-\frac{\sum_i^{occ} \varepsilon_i^{KS} \rho_i^{KS}(r)}{\rho^{KS}(r)}\right) \tag{18}$$

is very small in magnitude in all studied cases and negligible compared to $\Delta V_X(r)$ within the finite basis set used.

In Figure 3 are the HF and KS average local ionization energies for molecular nitrogen and carbon monoxide along the C_∞ axes. It is seen that $\bar{I}_{HF}(r)$ and $\bar{I}_{KS}(r)$ have similar shapes but do display significant differences, perhaps more pronounced than those observed for the atoms analyzed above. Figure 4 shows the difference between the HF and KS results, along with the BJ approximation $\Delta V_X^{BJ}(r)$, which again performs quite well, except for a consistent displacement in the case of N_2. This could possibly be related to the constant to which $\Delta V_X^{BJ}(r)$ should tend for large r, which we could not evaluate (vide supra). It is also possible that the very large basis set used for the potential affected its long-range behavior beyond the points we checked, because the set included extremely diffuse functions. In any case, the difference is uniform and the BJ approximation is still remarkably good.

Conclusions and Outlook

We have analyzed the connection between the HF and the exchange-only KS versions of the average local ionization energy. The results show that it is possible to "correct" the KS result (eq 15) to recover all the (approximate) physical significance of $\bar{I}_{HF}(r)$, which was the $\bar{I}(r)$ originally proposed based on the interpretation given by the HF Koopmans' theorem to the orbital energies. We have obtained a particularly intriguing result: one can go from the KS result to the HF without evaluating a nonlocal potential.

The observation that eq 18 is small in magnitude suggests that one could set up a system of equations to compute HF eigenvalues from KS eigenvalues and $\Delta V_X(r)$, for which quite accurate approximations exist. One only needs to take eq 15, use the definition of $\bar{I}_{HF}(r)$ on the left-hand side, and approximate the $\rho_i^{HF}(\mathbf{r})$ by the KS ones.

$$-\frac{\sum_i^{occ} \varepsilon_i^{HF} \rho_i^{KS}(r)}{\rho^{KS}(r)} \approx \Delta V_X(r) - \frac{\sum_i^{occ} \varepsilon_i^{KS} \rho_i^{KS}(r)}{\rho^{KS}(r)} \qquad (19)$$

By evaluation of this equation at a number of points equal to the number of eigenvalues, one can solve for the HF eigenvalues from a KS calculation without explicitly evaluating the nonlocal HF terms. This is particularly relevant because it has been argued that the KS eigenvalues do not correspond to the energy derivative with respect to the number of electrons in orbital-dependent energy functionals.[41] We have shown here how to avoid nonlocal operators in evaluating the so-called "derivative discontinuity" in exchange-only calculations, and we emphasize that $\Delta V_{XC}(r)$ is in general the sum of the discontinuity over the occupied orbitals.

The most relevant aspects of our work can be summarized as follows:

1. There exists a connection between $\bar{I}_{HF}(r)$ and $\bar{I}_{KS}(r)$. It is purely local and permits the computation of HF $\bar{I}(\mathbf{r})$ from KS calculations. Equation 19 may provide a way of evaluating the second term in the right-hand side of eq A15b in ref 41, i.e., the derivative discontinuity (which summed over all orbitals is our $\Delta V_{XC}(r)$).

2. We propose an alternative definition of $\bar{I}(r)$ as a functional of the electronic density without any explicit reference to orbitals.

3. We show that the BJ approximation for $\Delta V_X(r)$ works well for present purposes.

4. $\bar{I}(r)$ is shown to be invariant to unitary transformations of the orbitals, even though this may seem surprising based on definition, eq 2.

5. If $\Delta V_X(r)$ is positive everywhere (assuming the Slater potential is a lower bound to $v_X(r)$), it follows that $\bar{I}_{HF}(r) > \bar{I}_{KS}(r)\ \forall r \in R^3$ as observed earlier by Politzer et al.[15,31] Could something be said about the eigenvalues? Formal proof of the key assumption on the Slater potential would help in establishing bounds for the KS eigenvalues and their relationship to the HF.

6. A relationship is derived, within the HF framework, that links three important indices of reactivity, local temperature, electrostatic potential, and average local ionization energy, through the Slater potential. This complements an analogous expression in the KS framework that also includes $\Delta V_X(r)$.

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References and Notes

(1) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
(2) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
(3) Yang, W.; Parr, R. G.; Pucci, R. *J. Chem. Phys.* **1984**, *81*, 2862.
(4) Ayers, P. W.; Levy, M. *Theor. Chem. Acc.* **2000**, *103*, 353.
(5) Morell, C.; Grand, A.; Toro-Labbe, A. *J. Phys. Chem. A* **2005**, *109*, 205.
(6) Sjoberg, P.; Murray, J. S.; Brink, T.; Politzer, P. *Can. J. Chem.* **1990**, *68*, 1440.
(7) Koopmans, T. A. *Physica* **1933**, *1*, 104.
(8) Politzer; P.; Murray, J. S. In *Theoretical Aspects of Chemical Reactivity*; Toro-Labbe, A., Ed.; Elsevier: Amsterdam, 2007, Chapter 8, p 119.
(9) Politzer, P.; Murray, J. S.; Grice, M. E.; Brinck, T.; Ranganathan, S. *J. Chem. Phys.* **1991**, *95*, 6699.
(10) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968.
(11) Politzer, P.; Murray, J. S.; Grice, M. E. *Collect. Czech. Chem. Commun.* **2005**, *70*, 550.
(12) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.
(13) Mann, J. B.; Meek, T. L.; Allen, L. C. *J. Am. Chem. Soc.* **2000**, *122*, 2780.
(14) Mann, J. B.; Meek, T. L.; Knight, E. T.; Capitani, J. F.; Allen, L. C. *J. Am. Chem. Soc.* **2000**, *122*, 5132.
(15) Murray, J. S.; Abu-Awwad, F.; Politzer, P. *J. Mol. Struct.* **2000**, *501−502*, 241.
(16) Toro-Labbe, A.; Jaque, P.; Murray, J. S.; Politzer, P. *Chem. Phys. Lett.* **2005**, *407*, 143.
(17) Ayers, P. W.; Parr, R. G.; Nagy, A. *Int. J. Quantum Chem.* **2002**, *90*, 309.
(18) Ghosh, S. K.; Berkowitz, M.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 8028.
(19) Ghosh, S. K.; Balbas, L. C. *J. Chem. Phys.* **1985**, *83*, 5778.
(20) Jin, P.; Murray, J. S.; Politzer, P. *Co. Le.* **2007**, *3*, 373.
(21) Gritsenko, O.; van Leeuwen, R.; van Lenthe, E.; Baerends, E. J. *Phys. Rev. A* **1995**, *51*, 1944.
(22) della Sala, F.; Görling, A. *J. Chem. Phys.* **2001**, *115*, 5718.
(23) Krieger, J. B.; Li, Y.; Iafrate, G. J. *Phys. Lett. A* **1990**, *146*, 256.
(24) Kleinman, L. *Phys. Rev. B* **1994**, *49*, 14197.
(25) March, N. H. *Int. J. Quantum Chem.* **2005**, *101*, 494.
(26) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2006**, *124*, 221101.
(27) Staroverov, V. N. *J. Chem. Phys.* **2008**, *129*, 134103.
(28) Ivanov, S.; Levy, M. *J. Chem. Phys.* **2003**, *119*, 7087.
(29) Politzer, P.; Parr, R. G. *J. Chem. Phys.* **1974**, *61*, 4258.
(30) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859.
(31) Politzer, P.; Abu-Awwad, F. *Theor. Chem. Acc.* **1998**, *99*, 83.
(32) Yang, W.; Wu, Q. *Phys. Rev. Lett.* **2002**, *89*, 143002.
(33) Zhao, Q.; Morrison, R. C.; Parr, R. G. *Phys. Rev. A* **1994**, *50*, 2138.
(34) Staroverov, V. N.; Scuseria, G. E.; Davidson, E. R. *J. Chem. Phys.* **2006**, *124*, 141103.
(35) Heaton-Burgess, T.; Bulat, F. A.; Yang, W. *Phys. Rev. Lett.* **2007**, *98*, 256401.
(36) Levy, M.; Perdew, J. P. *Phys. Rev. A* **1985**, *32*, 2010.
(37) Ou-Yang, H.; Levy, M. *Phys. Rev. Lett.* **1990**, *65*, 1036.
(38) Ou-Yang, H.; Levy, M. *Phys. Rev. A* **1991**, *44*, 54.
(39) Bulat, F. A.; Heaton-Burgess, T.; Cohen, A. J.; Yang, W. *J. Chem. Phys.* **2007**, *127*, 174101.
(40) Teale, A. M.; De Proft, F.; Tozer, D. J. *J. Chem. Phys.* **2008**, *129*, 044110.
(41) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *Phys. Rev. B* **2008**, *77*, 115123.

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