Physical significance of local-density-functional-theory eigenvalues

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It is shown that Slater's transition-state technique often used with $X\alpha$ calculations generalizes trivially to any local density functional. This technique is shown to yield excellent electron-removal energies for several popular local density functionals. More importantly we interpret density-functional-theory eigenvalues as orbital electronegativities, demonstrating that they quantitatively agree with Mulliken's definition of electronegativity to better than 1% on average for atoms.

Eigenvalues of the local-density-functional and local-spin-density-functional Hamiltonians are notoriously ill described. Association of the eigenvalues with electron removal energies via Koopman's theorem ignores significant orbital relaxation contributions to the energy.[1] The lack of correspondence between these eigenvalues and physical electron-removal energies has led some to describe them as having no known physical meaning[2] while others have sought schemes to alter density-functional theory (DFT) (e.g., by self-interaction corrections[1,3] or nonlocal-density approximations)[2,4] so as to create an effective potential which yields eigenvalues equivalent to removal energies. These techniques admittedly succeed in improving the eigenvalues in their agreement with physical ionization potentials. However, physical significance has been ascribed to bare local-density-functional eigenvalues as defining an electronegativity scale consistent with Mulliken's definition of electronegativity.[5] Furthermore, it is well known that ionization potentials can be calculated in density-functional theory using Slater's transition-state technique.[6,7]

In this paper we first demonstrate the adequacy of the Slater's transition-state technique with numerical results for the first ionization potentials of the atoms helium through argon, comparing several local-spin-density functionals. We have also compared these results with ionization potentials calculated from total energy differences for the same density functionals. Secondly, we calculate the highest occupied, bare local-density-functional eigenvalues for these same elements. We show these eigenvalues to compare well with Mulliken's electronegativities as calculated from experimental spectroscopic values of ionization potentials (I) and electron affinity (A) using the formula:

$$X = \tfrac{1}{2}(I + A) , \qquad (1)$$

where X denotes Mulliken's electronegativity.

By way of review, Slater's transition-state scheme assumes that the variation of total energy with respect to occupation number is expandable in a Taylor series. It therefore allows for the existence of fractional occupation numbers, an assumption so commonplace that we will not justify it further. For mathematical convenience the total energy is expanded about a spin orbital with half occupancy:

$$E \mid_{n_i} = E \mid_{1/2} + \frac{\partial E}{\partial n_i} \bigg|_{1/2} (n_i - \tfrac{1}{2})$$
$$+ \frac{1}{2!} \frac{\partial^2 E}{\partial n_i^2} \bigg|_{1/2} (n_i - \tfrac{1}{2})^2 + \cdots . \qquad (2)$$

The electron removal energy can now be calculated

$$I = E(1) - E(0)$$
$$= \frac{\partial E}{\partial n_i} \bigg|_{1/2} + \frac{1}{24} \frac{\partial^3 E}{\partial n_i^3} \bigg|_{1/2} + \cdots . \qquad (3)$$

Taking advantage of the fact that in local-density theory the derivative of total energy with respect to occupation number is precisely the LD eigenvalue,[6]

$$\varepsilon_i \mid_{1/2} = \frac{\partial \langle E_{\text{LDA}} \rangle}{\partial n_i} \bigg|_{1/2} . \qquad (4)$$

This is Slater's well-known assertion that electron-removal energies can be expressed up to third-order accuracy by eigenvalues calculated at half occupancy. Arbitrary accuracy may be obtained through consideration of subsequent terms of odd order given that the particular local-density functional is of sufficient accuracy to allow such improvement. We show that the bare half-occupied eigenvalues yield local-spin-density approximation (LSDA) electron removal energies to better than 1% accuracy in general.

Our calculations were performed using a modified Herman-Skillman[8] (HS) program. The modifications to the program include the generalization to a spin polarized format to accommodate LSDA as well as LDA. The choice of LDA or LSDA affects the form of the exchange-correlation potential, the energy per particle, and the total energies with all other calculational details identical to the original (Herman-Skillman) programs. Latter-tail corrections were not employed. In all cases the calculations were for the spectroscopic neutral atom ground state, or ion ground-state terms. Of course, as previously described, the transition-state configuration was halfway between the neutral and ionic ground states.

Table I summarizes our results for atomic first ioniza-

TABLE I. LSDA electron removal energies in eV for the highest occupied states in He through argon using the KS, $X\alpha$, GL, and JMW functionals. ΔE_{total} values compared with transition-state (TS) values.

	Expt.[d]	Kohn-Sham[a]		$X\alpha$[b]		Gunnarsson-Lundqvist		Janak-Moruzzi-Williams[c]	
		$E^+ - E^0$	TS	$E^+ - E^0$	TS	$E^+ - E^0$	TS	$E^+ - E^0$	TS
He	24.581	22.07	22.60	23.54	24.23	24.52	24.88	24.30	24.59
Li	5.390	5.03	5.12	5.58	5.72	5.69	5.80	5.62	5.75
Be	9.321	7.64	7.79	8.24	8.43	9.08	9.19	9.01	9.07
B	8.296	7.56	7.46	8.50	8.41	8.87	8.76	8.71	8.61
C	11.265	10.78	10.66	12.01	11.90	12.17	12.00	11.94	11.81
N	14.545	14.01	13.87	15.46	15.33	15.46	15.26	15.19	15.03
O	13.615	11.87	11.77	12.68	12.60	14.01	14.10	13.83	13.85
F	17.422	16.26	16.13	17.35	17.23	18.32	18.27	18.07	17.99
Ne	21.559	20.50	20.36	21.79	21.66	22.53	22.41	22.23	22.10
Na	5.138	4.87	4.93	5.17	5.25	5.58	5.63	5.51	5.59
Mg	7.645	6.49	6.58	6.81	6.92	7.79	7.85	7.73	7.76
Al	5.985	5.16	5.12	5.57	5.53	6.23	6.18	6.12	6.08
Si	8.149	7.44	7.39	8.00	7.95	8.60	8.52	8.45	8.39
P	10.55	9.69	9.63	10.37	10.32	10.93	10.83	10.74	10.69
S	10.357	8.82	8.79	9.29	9.26	10.60	10.67	10.47	10.49
Cl	13.01	11.71	11.66	12.35	12.29	13.45	13.44	13.26	13.23
Ar	15.755	14.49	14.43	15.26	15.20	16.22	16.18	16.00	15.95
Average error (%) ΔE_{TOT} vs TS		1.0		1.1		0.88		0.78	
Average error (%) TS vs Expt.		9.6		4.7		4.2		2.8	

[a]Reference 7.
[b]Reference 9.
[c]Reference 11.
[d]Reference 12.

tion potentials calculated for several widely used density functions. The Kohn-Sham[8] (KS) (exchange only), X-alpha ($X\alpha$),[9] Gunnarsson-Lundqvist[10] (GL), and Janak-Moruzzi-Williams[11] (JMW) LSDA's have all been employed to calculate atomic total energies, ion total energies and transition state ionization potentials. We compare the transition-state results for ionization potentials with those determined by subtracting the LSDA ion total energy from the ground-state neutral-atom value. A measure of the error involved with truncating Slater's transition-state procedure at the first term (the eigenvalue at half occupancy) is the relative differences between these two energies. This comparison reveals errors on the order of 1% with slight improvement moving from KS—$X\alpha$—GL—JMW. The JMW LSDA has an average deviation of 0.8% between transition state and total energy ionization potentials. This relative error also shows a general improving trend with increasing atomic number.

Also included in Table I for comparison are experimental values for these atomic ionization potentials. It is obvious from the above discussion that both the total energy and transition-state-derived removal energies should be of similar accuracy when compared with experiment and indeed this is the case. The deviation of ionization potentials so derived, when compared with experiments,[12] is then an inherent measure of the accuracy of the particular LSDA. Our calculations show, as expected, that addition

of correlation yields dramatic improvement in the electron removal energies as compared with the exchange-only Kohn-Sham potential. Further gradual improvement in the ionization potentials is evident in moving from $X\alpha$ to GL to JMW, this presumably is related to the improvements in the correlation energy's density dependence in the same order. The JMW LSDA yields a very creditable 2.8% average deviation from experiment, for the first 18 elements of the Periodic Table. These results rival those of self-interaction corrected values[1] and, greatly improve the so-called post hoc corrections.[13]

Table II shows the extension of transition state calculations to deep-lying $1s$ core states. The error in these values compared with experiment are in all cases better than those of the ionization potentials from the highest occupied state. The data in Table II illustrate that the relative importance of the exchange-correlation potential is greatest for the highest occupied levels. Therefore, the first ionization potentials offer the most stringent test for the LSDA. Before leaving the subject of the transition state it should be noted that a rich literature exists describing the utility of this technique in molecular calculations (e.g., Ref. 15) especially with the $X\alpha$ potential.[16]

The transition-state technique is easily extended to excitations by displacing one half electron from the ground-state level to the excited-state level, the difference in their eigenvalues yielding the excitation energy. For example,

TABLE II. $K\alpha$ electron removal energies in eV for LSDA approximations.

	Expt. (Ref. 14)	Kohn-Sham	$X\alpha$	Gunnarsson-Lundqvist	Janak-Moruzzi-Williams
He	24.59	22.60	24.23	24.88	24.59
Li	64.39	61.64	64.34	64.34	63.98
Be	119.3	120.56	123.97	123.39	122.98
B	194	198.81	200.72	199.89	199.48
C		291.14	295.30	294.55	294.12
N		403.77	408.00	407.54	407.10
O		538.11	542.70	541.72	541.27
F		690.71	695.50	694.26	693.80
Ne	870.1	861.76	866.65	865.29	864.81
Na	1079.1	1069.02	1074.71	1072.68	1072.16
Mg	1311.2	1299.71	1305.99	1303.47	1302.93
Al	1567.0	1555.01	1561.90	1558.82	1558.27
Si	1846	1833.18	1840.60	1837.09	1836.53
P	2154	2134.45	2467.80	2463.52	2462.15
S	2477	2459.45	2467.80	2463.52	2462.15
Cl	2830	2807.59	2816.35	2811.70	2811.12
Ar	3203	3178.83	3187.97	3183.00	3182.40

the technique has recently been used with great success to calculate Auger excitation energies to iron.[17] Recently, Williams and Lang[18] have illustrated how the technique can be of use in examining core-level excitation energies in extended metallic systems.

We now review the more fundamental question of the interpretation of LSDA and LDA eigenvalues. Equation (4) describes the fact that the eigenvalues are precisely first derivatives of total energy with respect to occupation number. Stated succinctly in thermodynamic terms, the eigenvalues are Lagrange parameters associated with the minimization of total energy and as such, the eigenvalue represents the chemical potential of the orbital. As chemical potentials they offer a convenient and powerful electronegativity scale. This interpretation of orbital elec-

tronegativities as derivatives of total energies with respect to occupation agrees qualitatively with Pauling's[19] definition of electronegativity as the power of an atom to attract electrons to itself.

To elucidate this concept in a quantitative fashion we review the arguments set forth [by one of the authors (KHJ)] in Ref. 5. The definition of electronegativity as in Eq. (4) is analogous to that of Hinze et al.[20] as a generalization of Mulliken's electronegativity [Eq. (2)]. Again we can call upon Slater's Taylor-series expansion of the total energy (this time about $n_i = 0$) to calculate the ionization potential. The electron affinity is calculated in a similar fashion (the electron affinity is defined as the difference in total energy of the negative ion subtracted from the neutral atom ground state). This leads to the important rela-

TABLE III. Experimentally determined Mulliken electronegativities (in eV) compared with JMW LSDA eigenvalues (or HL LDA eigenvalues).

	Expt. ionization potential[a]	Expt. electron affinity[b]	$X = \frac{1}{2}(I + A)$	JMW eigenvalue	Error (%)
B	8.296	0.28	4.238	4.247	0.2
C	11.264	1.263	6.264	6.354	1.4
O	13.614	1.46	7.537	7.461	1.0
F	17.420	3.40	10.410	10.511	1.0
Al	5.984	0.44	3.212	3.162	1.6
Si	8.149	1.39	4.769	4.802	0.7
S	10.357	2.077	6.217	6.227	0.2
Cl	13.01	3.62	8.315	8.345	0.5
Li	5.390	0.618	3.004	2.956[d]	1.6
N	14.540	0[c]	7.270	7.329[d]	0.8
Na	5.138	0.548	2.843	2.898[d]	1.9
P	10.55	0.746	5.648	5.698[d]	0.9

[a]Reference 12.
[b]References 21 and 22.
[c]Reference 22.
[d]Hedin-Lundqvist eigenvalue (Ref. 23).

tionship for the electronegativity X_i of the ith state:

$$X_i = \tfrac{1}{2}(I_i + A_i) = \varepsilon_i \mid_0 + \frac{1}{24}\frac{\partial^3 E}{\partial n_i^3}\bigg|_0 + \cdots . \qquad (5)$$

Thus, to third-order terms in total energy the expression for Mulliken's electronegativity is satisfied by the LSDA (LDA) eigenvalue.

In Table III we compare highest occupied atomic eigenvalues of the JMW density function with experimentally derived values of Mulliken's electronegativity (i.e., from the sums of experimental ionization potentials[13,20] and electron affinities).[21,22] For those elements that do not have filled or half-filled subshells (B, C, O, F, Al, Si, S, Cl) the comparison is with LSDA eigenvalues. The substantial agreement between these values and experiment is taken as confirmation of this interpretation of the eigenvalues. For half-filled or filled subshells the analysis is a little more complicated in that the Pauli exclusion principle does not allow for additional electrons in these states. Therefore, experimentally derived electron affinities correspond to the lowest unoccupied orbitals. In the case of half-filled shells, for the sake of comparison it is possible to relax the exclusion principle by comparing experimental electronegativity values with spin-restricted (LDA) eigenvalues (where now the ionization potentials and electron affinity describe the same state since spin is no longer a quantum number). The JMW LSDA reduces to the Hedin-Lundqvist[23] (HL) LDA in its non-spin-polarized form. The calculated electronegativities for Li, N, Na, and P compare favorably with highest occupied HL eigenvalues.

Figure 1 illustrates the variation of the total energy of a sulfur atom as a function of the deviation of the $3p$ orbital occupancy from the $3p^4$ ground state as calculated using the JMW potential. This figure illustrates several poignant features relevant to the previous discussion. It shows the total energy to be a relatively smoothly varying function of occupation number. The chord connecting $E(-1)$ with $E(+1)$ obviously has slope $\tfrac{1}{2}(I + A)$ by definition of I and A. This chord is parallel to a line tangent to $E(n_i)$ at $n_i = 0$. Therefore $X = \tfrac{1}{2}(I + A)$. Further, the
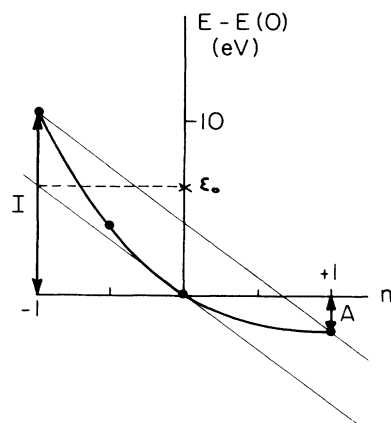

FIG. 1. Total energy versus occupational number for sulfur using the JMW LSDA. $X = \partial E / \partial n_i = \tfrac{1}{2}(I + A)$.

value of the slope is shown to be in good agreement with the calculated ground-state $3p$ eigenvalue.

We conclude that density-functional eigenvalues do have simple and important physical significance. While these eigenvalues do not correspond to electron removal energies, Slater's transition state offers a simple, widely applicable means for determining electron removal energies from local-density calculations. Further the transition state is easily generalized to the calculation of electron affinities and electron excitation energies. Though discussed here only for atoms, the electronegativity scale described by DFT eigenvalues is of wide importance in such areas as molecular bonding, charge transfer, covalency, etc. Much of the controversy over LDA eigenvalues can be put to rest through the fundamental distinction between eigenvalues (electronegativities) and removal energies (ionization potentials) in local DFT.

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