

GENERALIZED EXCHANGE LOCAL-SPIN-DENSITY-FUNCTIONAL THEORY: ONE-ELECTRON ENERGIES AND EIGENVALUES

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Received December 3rd, 1987

Accepted January 4th, 1988

To Rudolf Zahradnik who has always brought Joy and Wisdom to his work.

Within the Generalized Exchange (GX) LSD scheme, a method to calculate the ionization potential (IP) of an atom has been developed involving correction terms to the negative of the eigenvalue of the highest occupied atomic orbital (HOOA). These correction terms are evaluated non-iteratively using the fully occupied orbitals of the ground state of the neutral atom. Within the unrelaxed orbital approximation, this corrected eigenvalue IP , IP^{corr} , is completely equivalent to the Transition State IP , calculated from an SCF calculation at half-occupancy of the HOOA, when used with density-functional (DF) schemes that do not include self-interaction. The present scheme can also be used with self-interaction corrected DF schemes. In both cases, the corrected eigenvalue method of calculating IP 's gives good results. The techniques used to derive IP^{corr} are applied to derive an expression for the electronegativity of the free atom which can be used with both self-interaction and non-self-interaction corrected DF schemes. The results of IP and electronegativity calculations for the helium to krypton atoms are reported using a variety of DF schemes. These are compared to each other and to the experimental values whenever possible.

In Density-Functional theory, the total energy from Kohn and Sham¹ is

$$E^{DF} = \sum_i f_i \langle u_i(\mathbf{r}) | \mathbf{f}_r | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i,j} f_i f_j \langle u_i(\mathbf{r}) u_j(\mathbf{r}') | | u_i(\mathbf{r}) u_j(\mathbf{r}') \rangle + \frac{1}{2} \sum_i^s f_i \langle u_i(\mathbf{r}) | U_i^{xc}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + s' \text{ spin exchange term}, \quad (1)$$

where \mathbf{f}_r is the kinetic and nuclear attraction energy operator, $-\nabla_i^2 - 2Z/|\mathbf{r}|$, and $| |$ represent the inter-electronic repulsion operator, $2/|\mathbf{r} - \mathbf{r}'|$. The exchange-correlation density, $U_i^{xc}(\mathbf{r})$ in Eq. (1), is the single-particle exchange-correlation density^{2,3,4}. The total energy is minimized with respect to variation in the one-electron eigenfunctions, $u_i(\mathbf{r})$, preserving normalization,

$$\int n(\mathbf{r}) d\mathbf{r} = \sum_i^s f_i \langle u_i(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \sum_i^{s'} f_i \langle u_i(\mathbf{r}) | u_i(\mathbf{r}) \rangle = N_s + N_{s'} = N, \quad (2)$$

where N_s and $N_{s'}$ are the number of s and s' spin electrons, and N the total number of electrons. The total electron density $n(\mathbf{r})$ is¹

$$n(\mathbf{r}) = \sum_i^s f_i |u_i(\mathbf{r})|^2 + \sum_i^{s'} f_i |u_i(\mathbf{r})|^2. \quad (3)$$

Minimizing the total energy (1)

$$\{\mathbf{f}_r + \sum_i f_i \langle u_i(\mathbf{r}') | |u_i(\mathbf{r}') \rangle + V_k^{\text{xc}}(\mathbf{r})\} |u_k(\mathbf{r}) \rangle = \varepsilon_k |u_k(\mathbf{r}) \rangle, \quad (4)$$

where the one-electron potential, $V_k^{\text{xc}}(\mathbf{r})$, is

$$V_k^{\text{xc}}(\mathbf{r}) = \frac{1}{2} \partial \left[\sum_i^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{xc}}(\mathbf{r}) | u_i(\mathbf{r}) \rangle \right] / \partial n_k(\mathbf{r}) \quad (5)$$

when the k^{th} electron has spin s , and the one-electron density is

$$n_k(\mathbf{r}) = f_k |u_k(\mathbf{r})|^2. \quad (6)$$

Expression (4) is the one-electron eigenvalue equation to be solved self-consistently in Density-Functional theory; ε_k is the Lagrange multiplier in the minimization, the orbital eigenvalue.

Slater and Wood³ and Janak⁴ proved that ε_k is obtained directly from

$$(\partial E^{\text{DF}} / \partial f_k)_{f_k=1} = \varepsilon_k, \quad (7)$$

where f_k is the k^{th} orbital occupation number, one or zero. Thus the total energy is a *continuous function of the occupation numbers*. Although unphysical, it is a very powerful tool for calculating various types of one-electron energies. The one-electron exchange-correlation potential (5) using Eq. (7) gives

$$V_k^{\text{xc}}(\mathbf{r}) = \frac{1}{2} \partial \left[\sum_i^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{xc}}(\mathbf{r}) | u_i(\mathbf{r}) \rangle \right] / \partial f_k. \quad (8)$$

This expression is evaluated for f_k equal to one.

The LSD GX exchange² is rewritten to include any self-interaction corrected exchange densities⁵, this general GX exchange will be labelled GGX,

$$U_k^{\text{GGX}}(\mathbf{r}) = -9c\alpha^{\text{lim}} \{n_s(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} + \\ + [-f_k \langle u_k(\mathbf{r}') | |u_k(\mathbf{r}') \rangle]^{\text{SI/SIX/SIC}} + [9c\alpha^{\text{SI}} n_k^{1/3}(\mathbf{r})]^{\text{SI/LSD-SI/SIC}}. \quad (9)$$

The square bracket superscripts designate which term is present. Thus, the superscript SI/SIX in the second term of Eq. (9) means that the non-local self-interaction potential is present in the GX-SI and GX-SIX exchange densities⁵. For the GX-SIX and GX-LSD-SI exchange densities⁵, the B_1 parameter in the first term of Eq. (9) equals -1 . Table I gives the values of the parameters B_1 , B_2 , α^{lim} and α^{SI} for the various exchange densities. The α^{SI} in the GX-LSD-SI scheme is negative⁵.

Putting the GGX exchange (9) in the one-electron exchange potential (8) gives the GGX one-electron exchange potential

$$\begin{aligned}
 V_k^{\text{GGX}}(\mathbf{r}) = & -\frac{2}{3}\alpha^{\text{lim}}\{n_s(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} n_i(\mathbf{r}) - \frac{2}{3} \sum_i^s \{n_s(\mathbf{r}) + \\
 & + B_1 n_i(\mathbf{r})\} \{n_s(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) + \{n_s(\mathbf{r}) + 2B_1 n_k(\mathbf{r})\} \cdot \\
 & \cdot \{n_s(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} - \frac{2}{3} B_2 \{n_s(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} n_k(\mathbf{r}) + \\
 & + [-f_k \langle u_k(\mathbf{r}') | u_k(\mathbf{r}') \rangle]^{\text{SI/SIX/SIC}} + [6c\alpha^{\text{SI}} n_k^{1/3}(\mathbf{r})]^{\text{SI/LSD-SI/SIC}} \quad (10)
 \end{aligned}$$

which is used in the one-electron eigenvalue equation (4).

The LSD GX theory is a generalization of the $X\alpha$ theory, therefore the exchange potential (10) reduces to the $X\alpha$ exchange potential when homogeneous Fermi hole parameters are used: with B_1 and B_2 equal to zero

$$V^{X\alpha}(n_s(\mathbf{r})) = -6c\alpha^{\text{lim}} n_s^{1/3}(\mathbf{r}), \quad (11)$$

where α^{lim} equals 0.866173. Using the approximation

$$n_i(\mathbf{r})/n_s(\mathbf{r}) \cong 1/N_s \quad (12)$$

previously discussed^{2,5} the LSD GX exchange potential reduces to

$$V^{X\alpha}(n_s(\mathbf{r})) = -6c\alpha_s n_s^{1/3}(\mathbf{r}), \quad (13)$$

where α_s is a theoretically derived expression, a function of the total number of spin s electrons, N_s (refs^{2,6,7}), and depends on the Fermi hole parameters B_1 , B_2 and α^{lim} (refs^{2,5}).

The long range behaviour of the one-electron exchange potential must obey^{8,9}

$$\lim_{r \rightarrow \infty} rV^X(\mathbf{r}) = -2 \quad (14)$$

in Rydbergs, for the *inhomogeneous* electron gas. Consequently, if the exchange potential in Eq. (14) is written as the sum of self-interaction and pure-exchange components, the pure-exchange must approach zero, while the self-interaction must

approach -2 ,

$$\lim_{r \rightarrow \infty} r(V_i^{\text{SI}}(\mathbf{r}) + V_i^{\text{exc}}(\mathbf{r})) = \lim_{r \rightarrow \infty} rV_i^{\text{SI}}(\mathbf{r}) = -2. \quad (15)$$

Applying this limit to the GGX exchange potential (10) gives

$$\lim_{r \rightarrow \infty} rV_i^{\text{GGX}}(\mathbf{r}) = [-2]^{\text{SI/SIX/SIC}} \quad (16)$$

and zero for any other potential. Only the GX-SI and GX-SIX potentials, (or any potential corrected for self-interaction using the SIC scheme⁹ such as the SIC-FE exchange potential) contain the correct, non-local self-interaction potential which approaches the correct limit as r gets large.

TABLE I

The parameters B_1 , B_2 , α^{lim} and α^{SI} for the various theories discussed in refs^{2,5}

Theory	B_1	B_2	α^{lim}	α^{SI}
X α	0.0	0.0	variable	0.0
FE ^a	0.0	0.0	2/3	0.0
SIC-FE	0.0	0.0	2/3	2/3
GX/FEL ^b	3.178952	4.768428	2/3	0.0
GX/W ^b	2.514776	3.772148	0.698526	0.0
GX/GWB ^b	2.0	3.0	0.727539	0.0
GX/H ^b	0.0	0.0	0.866173	0.0
GX-SI/FEL	3.178952	4.768428	2/3	0.866173
GX-SI/W	2.514776	3.772147	0.698526	0.866173
GX-SI/GWB	2.0	3.0	0.727539	0.866173
GX-SI/H	0.0	0.0	0.866173	0.866173
GX-SIX/FEL	-1.0	4.768428	2/3	0.0
GX-SIX/W	-1.0	3.772147	0.698526	0.0
GX-SIX/GWB	-1.0	3.0	0.727539	0.0
GX-SIX/H	-1.0	0.0	0.866173	0.0
GX-LSD-SI/FEL	-1.0	4.768428	2/3	-0.866173
GX-LSD-SI/W	-1.0	3.772147	0.698526	-0.866173
GX-LSD-SI/GWB	-1.0	3.0	0.727539	-0.866173
GX-LSD-SI/H	-1.0	0.0	0.866173	-0.866173

^a Free electron gas exchange density; ^b free electron limit; Wigner⁶, Gopinathan, Whitehead and Bogdanovic⁷ and the Homogeneous Fermi Hole parameters².

THEORETICAL

Ionization Potentials

The ionization potential (IP) is the energy to remove an electron from an atom to infinity

$$IP = E^+ - E^0, \quad (17)$$

where E^+ is the positive ion total energy and E^0 the neutral atom energy. Using the GGX exchange, the neutral atom total energy, E^{GGX^0} , is

$$E^{\text{GGX}^0} = \sum_i f_i \langle u_i(\mathbf{r}) | \mathbf{f}_r | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i,j} f_i f_j \langle u_i(\mathbf{r}) u_j(\mathbf{r}') | | u_i(\mathbf{r}) u_j(\mathbf{r}') \rangle + \\ + \frac{1}{2} \sum_i^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^0}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_i^{s'} f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^0}(\mathbf{r}) | u_i(\mathbf{r}) \rangle, \quad (18)$$

where the single-particle exchange is given by Eq. (9). The total energy of the positive ion, E^{GGX^+} , is

$$E^{\text{GGX}^+} = \sum_{i \neq k} f_i \langle u_i(\mathbf{r}) | \mathbf{f}_r | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i,j \neq k} f_i f_j \langle u_i(\mathbf{r}) u_j(\mathbf{r}') | | u_i(\mathbf{r}) u_j(\mathbf{r}') \rangle + \\ + \frac{1}{2} \sum_{i \neq k}^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^+}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_i^{s'} f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^+}(\mathbf{r}) | u_i(\mathbf{r}) \rangle, \quad (19)$$

where the k^{th} electron, with spin s , has been removed. The ionization potential of the k^{th} electron is calculated by subtracting the total energy of the neutral species (Eq. (18)) from the total energy of the positive ion (Eq. (19)). Neglecting relaxation of orbitals upon ionization, terms common to the total energy equations of the positive and neutral species cancel. Hence,

$$IP_k = -f_k \langle u_k(\mathbf{r}) | \mathbf{f}_r | u_k(\mathbf{r}) \rangle - \sum_{i=k} f_k f_i \langle u_k(\mathbf{r}) u_i(\mathbf{r}') | | u_k(\mathbf{r}) u_i(\mathbf{r}') \rangle - \\ - \frac{1}{2} \sum_{i=k}^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^0}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i \neq k}^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^+}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \\ + \frac{1}{2} f_k^2 \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle, \quad (20)$$

where $\frac{1}{2} f_k^2 \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle$ has been added and subtracted in Eq. (20) to remove the $\neq k$ condition in the Coulomb repulsion term.

Writing the total positive ion electron density in terms of the total neutral atom electron density gives

$$n_s^+(\mathbf{r}) = n_s^0(\mathbf{r}) - n_k(\mathbf{r}). \quad (21)$$

Consequently the single-particle exchange density of the positive ion is

$$U_i^{\text{GGX}^+}(\mathbf{r}) = -9c\alpha^{\text{lim}}\{n_s^0(\mathbf{r}) - n_k(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) - n_k(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} + \\ + [-f_i \langle u_i(\mathbf{r}') | u_i(\mathbf{r}) \rangle]^{SI/SIX/SIC} + [9c\alpha^{SI} n_i^{1/3}(\mathbf{r})]^{SI/LSD-SI/SIC}. \quad (22)$$

The last factor in the first term can be expanded using the binomial theorem¹⁰, to give

$$\{n_s^0(\mathbf{r}) - n_k(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} = \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} \times \\ \times \{1 - n_k(\mathbf{r})/(n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r}))\}^{-2/3} = \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} \times \\ \times \{1 + \frac{2}{3} n_k(\mathbf{r})/(n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})) + \frac{5}{9} [n_k(\mathbf{r})/(n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r}))]^2 + \\ + (40/81) [n_k(\mathbf{r})/(n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r}))]^3 + \dots\} \quad (23)$$

substituting Eq. (23) in the *IP* equation (20), the resulting equation can be expressed in terms of the GGX eigenvalue equation defined by Eqs (4) and (10) and other terms expressed as brackets of powers of the wavefunction $u_k(\mathbf{r})$ and its corresponding occupation number f_k as

$$IP_k = -\varepsilon_k + [\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{GX/LSD-SI} + \\ + [\frac{2}{3} c\alpha^{SI} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} - \\ - \frac{9}{2} c\alpha^{\text{lim}} (1 + B_1) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle + \\ + \frac{9}{2} c\alpha^{\text{lim}} \frac{2}{3} (1 + B_2) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} | u_k^2(\mathbf{r}) \rangle + \\ + \frac{9}{2} c\alpha^{\text{lim}} \frac{2}{3} \langle u_k^2(\mathbf{r}) | \sum_{i \neq k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle - \\ - \frac{9}{2} c\alpha^{\text{lim}} \frac{5}{9} \langle u_k^2(\mathbf{r}) | \sum_{i \neq k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} | u_k^2(\mathbf{r}) \rangle + \\ + \frac{9}{2} c\alpha^{\text{lim}} \frac{5}{9} \langle u_k^3(\mathbf{r}) | \sum_{i \neq k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_k^3(\mathbf{r}) \rangle - \\ - \frac{9}{2} c\alpha^{\text{lim}} (40/81) \langle u_k^3(\mathbf{r}) | \sum_{i \neq k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-11/3} \times \\ \times \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} n_i(\mathbf{r}) | u_k^3(\mathbf{r}) \rangle, \quad (24)$$

where $u_k^3(\mathbf{r})$ terms are included, but $u_k^4(\mathbf{r})$ terms are not. The third term in Eq. (24)

is the IP-LSD-SI correction, the fourth term the 1st IP correction, the fifth term the 2nd IP correction, the sixth and seventh terms together the 3rd IP correction, and the eight and ninth terms the 4th IP correction. Equation (24) defines the *unrelaxed* IP.

The 4th IP correction is small, of the order of $[n_k(\mathbf{r})/n_s^0(\mathbf{r})]^3$, and can be neglected. Gopinathan¹⁰, using this approach to derive the relationship between the $X\alpha$ eigenvalue and the IP, found

$$IP_k = -\varepsilon_k^{X\alpha} + \frac{1}{2}\langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \quad (25)$$

which are the first two terms in Eq. (24). He assumed the remaining terms negligible. This is not true; in the non-self-interaction corrected LSD GX scheme, the 1st correction term has a specific role. If the expression

$$B_1 = \{\frac{1}{2} - A_1\}/A_1 \quad (26)$$

is substituted for B_1 , the result is the local self-interaction potential in the exchange density of the k^{th} electron⁵. This term *cancels* the approximate local self-interaction potential present in the one-electron exchange potential for the eigenvalue ε_k . This is then compensated by including the non-local self-interaction integral in the IP expression.

Therefore, the 1st IP correction to the eigenvalue ε_k is of the same order of magnitude as the self-interaction integral and not negligible. Nor is the 2nd IP correction, being of the same order of magnitude as the 1st IP correction, and hence, even though they have different signs, there is no reason to assume that they would not contribute significantly to the IP. Since the 3rd IP correction also varies as $n_k^2(\mathbf{r})$, it cannot be neglected.

It is useful to estimate the magnitude and sign of the corrections in the various schemes. The approximation

$$1/N_s \cong n_k(\mathbf{r})/n_s^0(\mathbf{r}) \quad (27)$$

as well as the B_1 , B_2 and α^{lim} parameters of the Homogeneous Fermi Hole will be used to simplify evaluation of terms in Eq. (24). This gives

$$\begin{aligned} IP_k \cong & -\varepsilon_k + \left[\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \right]^{\text{GX/LSD-SI}} + \\ & + \left[\frac{3}{2} \alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle \right]^{\text{SI/LSD-SI/SIC}} - \\ & - \frac{3}{2} \alpha^{\text{lim}} N_s^{-2/3} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle [-2(1 - 1/N_s)]^{\text{SIX/LSD-SI}} + \\ & + \frac{3}{2} \alpha^{\text{lim}} N_s^{-2/3} \langle u_k(\mathbf{r}) | n_s^{0/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle \frac{1}{3} (1 - 1/N_s) [1 + 5/N_s]^{\text{SIX/LSD-SI}}. \end{aligned} \quad (28)$$

The corrections in this equation can be expressed in terms of the self-interaction integral using the inequality of Gadre, Bartolotti and Handy^{5,9,11}

$$\frac{1}{2} \sum_{i,j} f_i f_j \langle u_i(\mathbf{r}) u_j(\mathbf{r}') | | u_i(\mathbf{r}) u_j(\mathbf{r}') \rangle \leq 2.184 N^{-2/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r} \quad (29)$$

and hence.

$$IP_k = -\varepsilon_k + \{A + BN_s^{-2/3}\} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle, \quad (30)$$

where A is a constant, and B depends on the total number of spin s electrons N_s . Table II gives the values of A and B for the various schemes. To compare the effect of the corrections to the eigenvalue in the different schemes, the factor $\{A + BN_s^{-2/3}\}$ has been plotted versus N_s , the number of spin s electrons, Fig. 1. The negative of the LSD GX and LSD FE eigenvalues have the largest corrections; neither scheme contains the correct local, or non-local, self-interaction potential. The largest correction is the exact, non-local, self-interaction potential since it contributes the coefficient A equal to $1/2$. The negative of the GX-LSD-SI eigenvalue has smaller corrections even though the largest correction is the exact self-interaction potential, because the latter is partially cancelled by the IP-LSD-SI correction. The negative of the SIC-FE and GX-SI eigenvalue have smaller corrections and the negative of the GX-SIX eigenvalue has the smallest corrections for large atoms, with a limiting value of zero.

Similar^{9,10} comparisons have been made for the $X\alpha$ and SIC-FE schemes, assuming the $BN_s^{-2/3}$ portion of the corrections negligible. This term is smaller than A but not negligible.

Relaxation Effect and the Ionization Potential

In Density-Functional theory, the eigenvalue of the k^{th} electron is obtained from Eq. (7) (refs^{3,4}). Also the IP can be calculated from Eq. (9)

$$IP = E^+ - E^0 = - \int_0^1 \varepsilon_k df_k. \quad (31)$$

The exact evaluation of this integral accounts for the relaxation of the orbitals upon ionization, and defines the *relaxed IP*.

In the Hartree-Fock theory, neglecting relaxation, the eigenvalue is independent of the occupation number, f_k , and the integral (31) becomes

$$IP_k^{\text{nr}} = -\varepsilon_k, \quad (32)$$

ur means unrelaxed and r relaxed. Equation (32) is Koopmans' theorem, and gives

an approximation to the IP from a single, self-consistent field (SCF) calculation. There are no correction terms.

In the non-self-interaction corrected LSD theory, the eigenvalue ε_k depends heavily on the occupation number of the k^{th} orbital, f_k , through the *Coulomb and Exchange* terms because the self-interaction energy is not exactly cancelled. Evaluating the integral (31) is difficult. An approximation is

$$IP_k^r \cong -1/2[\varepsilon_k(f_k = 1) + \varepsilon_k(f_k = 0)]. \quad (33)$$

TABLE II

Values of A and B for the factor $\{A + BN_s^{-2/3}\}$ in the expression for the unrelaxed IP given by Eq. (30)

Scheme	A	B
GX	0.5	$-0.062[2 + 1/N_s]$
FE	0.5	$-0.47[2 + 1/N_s]$
GX-LSD-SI	0.315	$0.062[1 - 1/N_s][7 + 5/N_s]$
GX-SI	0.185	$-0.062[2 + 1/N_s]$
SIC-FE	0.142	$-0.047[2 + 1/N_s]$
GX-SIX	0.0	$0.062[1 - 1/N_s][7 + 5/N_s]$

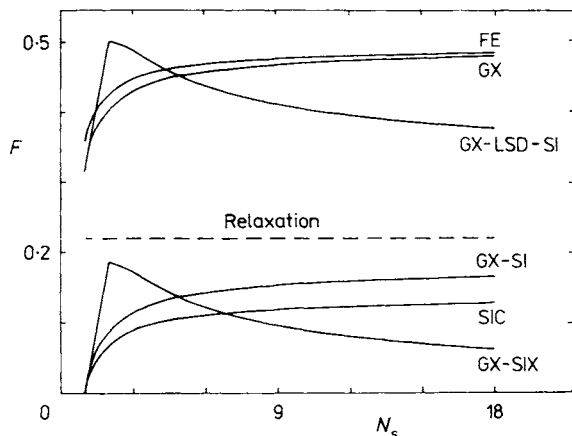


FIG. 1

The factor $F = \{A + BN_s^{-2/3}\}$ for the LSD GX, LSD FE, GX-LSD-SI, GX-SI, SIC-FE and GX-SIX schemes versus N_s , the number of spin s electrons, for N_s equal 1 to 18

A further approximation can be made by defining a "transition state" as^{12,13}

$$IP_k^r \cong -\varepsilon_k(f_k = \frac{1}{2}), \quad (34)$$

where the k^{th} eigenvalue is from a single SCF calculation with a half-occupied k^{th} orbital¹⁴, the *Slater Transition State* (TS). Equation (34) was also derived for the HF theory by Hedin and Johansson¹⁵, and, calculations by Brandi, de Matos and Ferreira¹⁶ show that the concept of the Transition State is *numerically* valid, even in the HF theory.

The correct, relaxed IP should be calculated by subtracting the total energy of the neutral atom from the SCF total energy of the positive ion

$$IP_k^r = E_r^+ - E^0. \quad (35)$$

The relationship between the relaxed and unrelaxed IP 's is therefore

$$IP_k^r = IP_k^{\text{ur}} + R_k, \quad (36)$$

where IP_k^{ur} is given by Eq. (17) and

$$R_k = E_r^+ - E_{\text{ur}}^+. \quad (37)$$

E_r^+ is lower than E_{ur}^+ because the SCF total energy is the minimum energy of the positive ion, and therefore, the relaxation correction, R_k , is negative.

To compare the effects of the relaxation correction on the various schemes, the simplified IP_k^{ur} expression derived above, together with an approximate expression for the relaxation energy, is used.

Gopinathan¹⁰ empirically determined

$$R_k \cong -0.44 \left\{ \frac{1}{2} f_k^2 \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \right\}. \quad (38)$$

Assuming this relaxation energy to be similar for every scheme, it can be added to the expression for the IP^{ur} (Eq. (30)) to give the IP^r

$$IP_k^r \cong -\varepsilon_k + \{A' + BN_s^{-2/3}\} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle, \quad (39)$$

where A' equals $A - 0.22$. The values of A' and B for the various schemes are in Table III. The effect of the relaxation energy on the factors $\{A' + BN_s^{-2/3}\}$ for these schemes is shown in Fig. 1; the curves must be compared to the new baseline, labelled "relaxation", which has the net effect of shifting down the vertical scale by 0.22.

The negative of the eigenvalue in the GX-SI and SIC-FE schemes are a good approximation to the *relaxed IP* for N_s greater than 4, because the relaxation energy is

nearly cancelled by the *IP* correction terms; the negative of the GX-SI eigenvalue is a slightly better approximation to its relaxed *IP* than the SIC-FE eigenvalue is to its relaxed *IP*. This is also true of the GX-LSD-SI eigenvalue for large N_s values, but not of the LSD GX, LSD FE and GX-SIX eigenvalues.

For large N_s , the full set of correction terms approaches -0.035 , -0.078 and 0.095 in the GX-SI, SIC-FE and GX-LSD-SI schemes. Therefore the negative of the GX-SI eigenvalue is a slightly better approximate relaxed *IP* for systems with a large number of electrons.

The difference between the original baseline, of Fig. 1, and the dashed, relaxation baseline is the approximate relaxation correction in HF theory, since the unrelaxed HF *IP* contains no correction terms to the negative of its eigenvalue, and the full set of correction terms to the negative of the GX-SIX eigenvalue approaches this limit asymptotically. Consequently, even though the negative of the GX-SIX eigenvalue is *not a good approximation to the relaxed IP*, it is *a good approximation to the unrelaxed IP*, and is the only scheme in which Koopmans' theorem can be used, albeit approximately.

Transition State Eigenvalue

IP^{ur} was derived from the definition of *IP* in the section "Ionization Potentials" (hereafter referred to as Section II). In the previous section (Section III), the negative of the eigenvalue in the GX-LSD-SI, SIC-FE and GX-SI schemes approximated well the IP^r because the correction terms nearly cancelled the relaxation energy. However, the negative of the LSD GX and LSD FE eigenvalues are not good approximations to either IP^r or IP^{ur} because the total, local or non-local, self-interaction potential is absent from the exchange potential. Finally, the negative of the GX-SIX eigenvalue is a good approximation to IP^{ur} , and, obeys Koopman's theorem.

TABLE III

Values of A' and B for the factor $\{A' + BN_s^{-2/3}\}$ in the expression for the relaxed *IP* given by Eq. (34)

Scheme	A'	B
GX	0.280	$-0.062[2 + 1/N_s]$
FE	0.280	$-0.047[2 + 1/N_s]$
GX-LSD-SI	0.095	$0.062[1 - 1/N_s][7 + 5/N_s]$
GX-SI	-0.350	$-0.062[2 + 1/N_s]$
SIC-FE	-0.078	$-0.047[2 + 1/N_s]$
GX-SIX	-0.220	$0.062[1 - 1/N_s][7 + 5/N_s]$

These conclusions use the fully occupied k^{th} orbital to derive expressions relating the IP and the eigenvalue. The expression for the Transition State eigenvalue for a half-occupied k^{th} orbital (Eq. (34)) can be evaluated in the *unrelaxed orbital approximation* to relate it to the fully occupied orbital eigenvalue.

The transition state electron densities can be written in terms of the densities of the neutral atom as

$$n_k^{\dagger}(\mathbf{r}) = \frac{1}{2}n_k^{\circ}(\mathbf{r}) \quad (40)$$

and

$$n_s^{\dagger}(\mathbf{r}) = n_s^{\circ}(\mathbf{r}) - \frac{1}{2}n_k^{\circ}(\mathbf{r}). \quad (41)$$

The superscript \circ indicates an electron density at full occupancy of the k^{th} orbital, f_k equals 1. Evaluating the partial derivative of the total Energy expression at f_k equal $\frac{1}{2}$ and using Eqs (40) and (41) as well as the same approach as in Section II gives the TS eigenvalue, ε_k^{\dagger} ,

$$\begin{aligned} \varepsilon_k^{\dagger} = & \varepsilon_k + \left[-\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \right]^{\text{GX/LSD-SI}} + \\ & + \left\{ \left(\frac{1}{2} \right)^{1/3} - 1 \right\} \left[6c\alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{\circ 1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle \right]^{\text{SI/LSD-SI/SIC}} + \\ & + \frac{2}{3} c\alpha^{\text{lim}} (1 + B_1) \langle u_k^2(\mathbf{r}) | \{ n_s^{\circ}(\mathbf{r}) + B_2 n_k^{\circ}(\mathbf{r}) \}^{-2/3} | u_k^2(\mathbf{r}) \rangle - \\ & - \frac{2}{3} c\alpha^{\text{lim}} \frac{2}{3} (1 + B_2) \langle u_k^2(\mathbf{r}) | \{ n_s^{\circ}(\mathbf{r}) + B_1 n_s^{\circ}(\mathbf{r}) + B_1 n_k^{\circ}(\mathbf{r}) \} \times \\ & \times \{ n_s^{\circ}(\mathbf{r}) + B_2 n_k^{\circ}(\mathbf{r}) \}^{-5/3} | u_k^2(\mathbf{r}) \rangle - 3^{\text{rd}} IP \text{ corr.} \end{aligned} \quad (42)$$

The fourth and fifth terms in Eq. (42) are exactly the negative of the 1st and 2nd IP correction terms in Eq. (24) of Section II. The coefficient of the third term in Eq. (42) can be written as a fraction of the IP -LSD-SI correction term also in Eq. (24).

$$\begin{aligned} \varepsilon_k^{\dagger} = & \varepsilon_k + \left[-\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \right]^{\text{GX/LSD-SI}} - \\ & - 0.825 \left[IP\text{-LSD-SI corr.} \right]^{\text{SI/LSD-SI/SIC}} - 1^{\text{st}} IP \text{ corr.} - \\ & - 2^{\text{nd}} IP \text{ corr.} - 3^{\text{rd}} IP \text{ corr.} \end{aligned} \quad (43)$$

The eigenvalue of the TS can now be expressed in terms of the unrelaxed IP (Eq. (24)) as

$$\varepsilon_k^{\dagger} = -IP_k^{\text{ur}} + 0.175 \left[IP\text{-LSD-SI corr.} \right]^{\text{SI/LSD-SI/SIC}}. \quad (44)$$

The terms on the right-hand-side are evaluated for a fully occupied k^{th} orbital.

Using the inequality (29) to express the last factor in this expression in terms of the self-interaction integral, shows that this term equals zero in the LSD GX, LSD FE,

and GX-SIX schemes and -0.032 , 0.032 , and 0.025 times the self-interaction integral in the GX-LSD-SI, GX-SI, and SIC-FE schemes and hence to a good approximation, it can be neglected.

Consequently, in the LSD GX and LSD FE schemes, the difference between the TS and fully occupied orbital eigenvalues from Eq. (43) is, to a first approximation, *half the self-interaction integral*, which is the same result that Gopinathan¹⁰ obtained for the $X\alpha$ theory. Therefore, for these schemes, the calculation of the TS eigenvalue seems to be a way of *correcting for the self-interaction potential* which is not present in the one-electron exchange potential.

In the GX-SIX scheme, this difference is approximately equal to zero, and as in the HF theory, the eigenvalue in the unrelaxed orbital approximation is independent of the occupation number, confirming Koopmans' theorem in the GX-SIX scheme. In the GX-SI, SIC-FE and GX-LSD-SI schemes, the eigenvalue difference is equal to the negative of the *IP* correction terms which are a good approximation to the relaxation energy discussed in Section III.

Electron Affinity

The electron affinity (*EA*) is the energy to remove an electron from a negative ion to infinity

$$EA_m = E^0 - E^- . \quad (45)$$

The extra electron is in the m^{th} orbital and the total electron density can be expressed as

$$n_s^-(\mathbf{r}) = n_s^0(\mathbf{r}) + n_m(\mathbf{r}) \quad (46)$$

where $n_s^0(\mathbf{r})$ is the neutral atom total electron density. The derivations in Section II and in the previous section (Section IV) can be repeated to give a set of similar equations in terms of the total electron density of the negative ion; the one-electron operators are of the negative ion. The *EA* expressions will be re-expressed in terms of the one-electron operators of the neutral atom, for two reasons: firstly, the most convenient reference point for the various one-electron eigenvalues and energies is the neutral atom total energy, and secondly, this approach is essential for deriving expressions for the electronegativity.

The total energy of the negative ion is

$$E^{\text{GGX}^-} = \sum_{i \neq m} f_i \langle u_i(\mathbf{r}) | \mathbf{f}_r | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i, j \neq m} f_i f_j \langle u_i(\mathbf{r}) u_j(\mathbf{r}') | | u_i(\mathbf{r}) u_j(\mathbf{r}') \rangle + \\ + \frac{1}{2} \sum_{i=m}^s f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^-}(\mathbf{r}) | u_i(\mathbf{r}) \rangle + \frac{1}{2} \sum_{i=1}^{s'} f_i \langle u_i(\mathbf{r}) | U_i^{\text{GGX}^-}(\mathbf{r}) | u_i(\mathbf{r}) \rangle .$$

This gives,

$$\begin{aligned}
 EA_m = & - \langle u_m(\mathbf{r}) | \mathbf{f}_r + \sum_{j \neq m} f_j \langle u_j(\mathbf{r}') | u_j(\mathbf{r}') \rangle - \\
 & - \frac{2}{3} c\alpha^{\text{lim}} \left\{ \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} n_i(\mathbf{r}) - \frac{2}{3} \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \times \right. \\
 & \times \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) + \{n_s^0(\mathbf{r}) + 2B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} - \\
 & - \frac{2}{3} B_2 \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} n_m(\mathbf{r}) + \\
 & + [6c\alpha^{\text{SI}} n_m^{1/3}(\mathbf{r})]^{\text{SI/LSD-SI/SIC}} |u_m(\mathbf{r})\rangle - [\frac{1}{2} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | |u_m(\mathbf{r}) u_m(\mathbf{r}')\rangle]^{\text{GX/LSD-SI}} + \\
 & + [\frac{2}{3} c\alpha^{\text{SI}} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r})\rangle]^{\text{SI/LSD-SI/SIC}} + \\
 & + \frac{2}{3} c\alpha^{\text{lim}} (1 - B_1) \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} | u_m^2(\mathbf{r}) \rangle - \\
 & - \frac{2}{3} c\alpha^{\text{lim}} \frac{2}{3} (1 - B_2) \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m^2(\mathbf{r}) \rangle - \\
 & - \frac{2}{3} c\alpha^{\text{lim}} \frac{2}{3} \langle u_m^2(\mathbf{r}) | \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle + \\
 & + \frac{2}{3} c\alpha^{\text{lim}} \frac{5}{9} \langle u_m^2(\mathbf{r}) | \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle .
 \end{aligned} \tag{47}$$

The operator in the first bra-ket is equal to the *neutral atom one-electron eigenvalue operator for the mth orbital*, and hence, this term is not equal to the eigenvalue of the *mth orbital* ϵ_m . The third, fourth, fifth, sixth, and seventh terms together are the equivalents of the *IP-LSD-SI*, 1st, 2nd, and 3rd *IP* correction terms, respectively, defined in Eq. (28), for the *mth orbital*, and will be referred to as the *EA-LSD-SI*, 1st, 2nd, and 3rd *EA* correction terms, respectively.

Finally, it is convenient to define a pseudo-eigenvalue, ϵ'_m , as

$$\begin{aligned}
 \epsilon'_m + \langle u_m(\mathbf{r}) | \mathbf{f}_r + \sum_{j \neq m} f_j \langle u_j(\mathbf{r}') | u_j(\mathbf{r}') \rangle - \frac{2}{3} c\alpha^{\text{lim}} \left\{ \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} n_i(\mathbf{r}) - \right. \\
 - \frac{2}{3} \sum_{i \neq m}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) + \\
 + \{n_s^0(\mathbf{r}) + 2B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} - \frac{2}{3} B_2 \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \times \\
 \times \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} n_m(\mathbf{r}) + [6c\alpha^{\text{SI}} n_m^{1/3}(\mathbf{r})]^{\text{SI/LSD-SI/SIC}} + \\
 \left. + [-\langle u_{mk}(\mathbf{r}') | |u_m(\mathbf{r}')\rangle]^{\text{SI/SIX/SIC}} |u_m(\mathbf{r})\rangle \right\}
 \end{aligned} \tag{48}$$

so that the EA expression can be rewritten as

$$EA_m = -\varepsilon'_m - [2]^{SI/SIX/SIC} \frac{1}{2} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle + \\ + [\frac{3}{2} c\alpha^{SI} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} + 1^{st} EA \text{ corr.} + \\ + 2^{nd} EA \text{ corr.} + 3^{rd} EA \text{ corr.}, \quad (49)$$

where the $[2]^{SI/SIX/SIC}$ factor in the second term equals one and not zero in the LSD GX and GX-LSD-SI schemes.

The EA has been written in this form because, in the unrelaxed orbital approximation, for some open shell atoms such as boron and fluorine, the pseudo-eigenvalue ε'_m will exactly equal the eigenvalue of the k^{th} orbital of the neutral atom, which means that under these conditions the difference between the IP , given by Eq. (28), and the EA is, to a first approximation, *the self-interaction integral in all schemes*.

Electronegativity of Free Atoms

The electronegativity of a free atom is a measure of the power of an atom to attract an electron. Mulliken¹⁷⁻¹⁹ defined the electronegativity of an atom as the average of the IP and EA

$$\chi = \frac{1}{2} \{ IP + EA \}. \quad (50)$$

In the unrelaxed orbital approximation, this expression can be evaluated using the equations for the IP and EA (Eqs (28) and (49), respectively),

$$\chi = -\frac{1}{2}(\varepsilon_k + \varepsilon'_m) + [\frac{1}{4} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{GX/LSD-SI} - \\ - [2]^{SI/SIX/SIC} \frac{1}{4} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle + [\frac{3}{4} c\alpha^{SI} \{ \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle + \\ + \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle \}]^{SI/LSD-SI/SIC} - \frac{9}{4} c\alpha^{lim} \{ (1 + B_1) \langle u_k^2(\mathbf{r}) | \times \\ \times \{ n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r}) \}^{-2/3} | u_k^2(\mathbf{r}) \rangle - (1 - B_1) \times \\ \times \langle u_m^2(\mathbf{r}) | \{ n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r}) \}^{-2/3} | u_m^2(\mathbf{r}) \rangle \} + \frac{9}{4} c\alpha^{lim} \frac{2}{3} \{ (1 + B_2) \times \\ \times \langle u_k^2(\mathbf{r}) | \{ n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r}) \} \{ n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r}) \}^{-5/3} | u_k^2(\mathbf{r}) \rangle - \\ - (1 - B_2) \langle u_m^2(\mathbf{r}) | \{ n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r}) \} \{ n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r}) \}^{-5/3} | u_m^2(\mathbf{r}) \rangle \} + \\ + \frac{9}{4} c\alpha^{lim} \frac{2}{3} \langle u_k^2(\mathbf{r}) | \sum_{i \neq k}^6 \{ n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r}) \}^{-5/3} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle -$$

$$\begin{aligned}
& - \langle u_m^2(\mathbf{r}) | \sum_{i \neq m}^{s'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle - \\
& - \frac{9}{4} \alpha^{\text{lim}} \frac{5}{9} \langle u_k^2(\mathbf{r}) | \sum_{i \neq k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle - \\
& - \langle u_w^2(\mathbf{r}) | \sum_{i \neq m}^{s'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle, \quad (51)
\end{aligned}$$

where the last four terms will be small.

For open shell atoms, which have k^{th} and m^{th} orbitals with the same principal, and azimuthal quantum numbers and spin, these terms cancel exactly in the unrelaxed orbital approximation; the pseudo-eigenvalue ϵ'_m will equal the orbital eigenvalue ϵ_k . Therefore the electronegativity is

$$\begin{aligned}
\chi^{\text{op}} = & -\epsilon_k + [-\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{\text{SI/SIX/SIC}} + \\
& + [\frac{3}{2} \alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{\text{SI/LSD-SI/SIC}} + \\
& + \frac{9}{2} \alpha^{\text{lim}} B_1 \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle + \\
& + \frac{9}{2} \alpha^{\text{lim}} \frac{3}{2} B_2 \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle - \\
& - \frac{9}{4} \alpha^{\text{lim}} \frac{3}{2} \langle u_k^3(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^3(\mathbf{r}) \rangle + \\
& + \frac{9}{4} \alpha^{\text{lim}} \frac{5}{9} \langle u_k^3(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} | u_k^3(\mathbf{r}) \rangle. \quad (52)
\end{aligned}$$

The last two terms in Eq. (52) are from the incomplete cancellation of the terms in the summations of the last two terms of Eq. (51), but since they are of the order of $u_k^3(\mathbf{r})$, they will be neglected.

Clearly, the negative of the fully occupied orbital eigenvalue in the LSD GX and LSD FE schemes is, approximately, the electronegativity of the free atom. This is the same result that Bartolotti, Gadre and Parr¹⁸ and Manoli and Whitehead¹⁹ derived for the $X\alpha$ theory. The method used by the latter authors is the same as the one used in this work, but this work includes the correction terms to the IP , EA and electronegativity.

For discussion purposes, the theories in this work divide into two classes: the theories which contain the exact, non-local self-interaction integral (the GX-SI, GX-SIX and SIC schemes) will be the SI theories, while the schemes which have a completely local exchange potential (the LSD GX, LSD FE, $X\alpha$ and GX-LXD-SI schemes) will be the LSD theories. The electronegativity in these theories will be discussed for open and closed shell atoms.

Since DF theory allows the use of non integer occupation numbers of the orbitals^{3,12,20-22}, it is possible to find a transition state of the atom that can be used to calculate the electronegativity directly. Clearly, since Mulliken's definition of the electronegativity (50) defines the electronegativity as the average of the *IP* and *EA*, and, since the *IP* in the LSD schemes is given by a transition state which has a half-occupied k^{th} orbital, while the *EA* is given by a transition state with a half-occupied m^{th} orbital, then the eigenvalue of the neutral ground state of the atom should correspond to the average of the negative of the *IP* and *EA*, the electronegativity. This is the argument of Bartolotti, Gadre and Parr²⁰ for the electronegativity in the $X\alpha$ theory. The situation is not as straightforward for the other schemes discussed in this work, however a transition state can be found whose eigenvalue corresponds directly to the negative of the electronegativity.

The transition state used to calculate the electronegativity must reflect the characteristics of *IP* and *EA*. Consider an electronegativity transition state (χ -TS) where a portion of an electron is removed from the highest occupied atomic orbital (HOAO), k^{th} orbital, and placed in the lowest unoccupied atomic orbital (LUAO), m^{th} orbital, by Hund's rules. These partial electrons either do or do not have the same spin.

The Electronegativity Transition State Involving Partial Electrons with Parallel Spins

The k^{th} and m^{th} orbitals have the same spin. Therefore, neglecting the orbital relaxation, this implies

$$n_s^t(\mathbf{r}) = n_s^0(\mathbf{r}) - n_k(\mathbf{r}) + n_{k'}(\mathbf{r}) + n_m(\mathbf{r}) \quad (53)$$

$$n_{k'}(\mathbf{r}) = f_{k'} n_k(\mathbf{r}) \quad (54)$$

and

$$n_{m'}(\mathbf{r}) = f_{m'} n_m(\mathbf{r}) \quad (55)$$

since the occupation numbers of the fully occupied k^{th} and m^{th} orbitals, f_k and f_m respectively, equal one. In addition

$$f_{k'} + f_{m'} = 1 \quad (56)$$

to conserve the charge in the χ -TS.

The eigenvalues of the partial electrons can now be calculated from Eq. (7) and the approach used in Sections II and III gives

$$\begin{aligned} \varepsilon_{m'}^t &= \varepsilon_m' + (f_{k'} - 1) \langle u_m(\mathbf{r}) u_k(\mathbf{r}') | | u_m(\mathbf{r}) u_k(\mathbf{r}') \rangle + \\ &+ [f_{m'}]^{GX/LSD-SI} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle + \end{aligned}$$

$$\begin{aligned}
& + (f_m^{1/3} - 1) [6c\alpha^{SI} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} - \\
& - \frac{2}{3} c\alpha^{lim} (f_k - 1) \langle u_m(\mathbf{r}) u_k(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} - \\
& - \frac{2}{3} \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_m(\mathbf{r}) u_k(\mathbf{r}) \rangle - \\
& - \frac{2}{3} c\alpha^{lim} (f_k - 1) \langle u_m(\mathbf{r}) u_k(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} - \\
& - \frac{2}{3} \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m(\mathbf{r}) u_k(\mathbf{r}) \rangle - \\
& - \frac{2}{3} c\alpha^{lim} 2[B_2(f_m - 1) + f_m] \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} | u_m^2(\mathbf{r}) \rangle + \\
& + \frac{2}{3} c\alpha^{lim} 2[B_1(f_m - 1) + f_m] \frac{2}{3} \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \times \\
& \times \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m^2(\mathbf{r}) \rangle + \frac{2}{3} c\alpha^{lim} 2(f_k - 1) \times \\
& \times \langle u_m(\mathbf{r}) u_k(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k', m'=k}^2 \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \frac{5}{9} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + \\
& + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_m(\mathbf{r}) u_k(\mathbf{r}) \rangle + \\
& + \frac{2}{3} c\alpha^{lim} 2f_m \langle u_m^2(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} - \\
& - \frac{5}{9} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} | u_m^2(\mathbf{r}) \rangle, \quad (57)
\end{aligned}$$

where ε'_m is defined by Eq. (46). The χ -TS eigenvalue of the k^{th} electron can be calculated in a similar manner.

$$\begin{aligned}
\varepsilon_{k'}^t & = \varepsilon_k + f_m \langle u_k(\mathbf{r}) u_m(\mathbf{r}') | | u_k(\mathbf{r}) u_m(\mathbf{r}') \rangle + \\
& + [(f_k - 1) \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{GX/LSD-SI} + \\
& + (f_k^{1/3} - 1) [6c\alpha^{SI} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} - \\
& - \frac{2}{3} c\alpha^{lim} 2(B_1 + 1)(f_k - 1) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle + \\
& + \frac{2}{3} c\alpha^{lim} 2(B_2 + 1)(f_k - 1) \frac{2}{3} \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \times \\
& \times \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle - \frac{2}{3} c\alpha^{lim} f_m \times \\
& \times \langle u_k(\mathbf{r}) u_m(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} - \frac{2}{3} \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \times \\
& \times \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_k(\mathbf{r}) u_m(\mathbf{r}) \rangle - \frac{2}{3} c\alpha^{lim} f_m \times
\end{aligned}$$

$$\begin{aligned}
& \times \langle u_k(\mathbf{r}) u_m(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} - \frac{2}{3} \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \times \\
& \quad \times \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k(\mathbf{r}) u_m(\mathbf{r}) \rangle + \\
& \quad + \frac{9}{2} \alpha^{\text{lim}} 2(f_{k'} - 1) \langle u_k^2(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \\
& \quad - \frac{5}{9} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle + \\
& \quad + \frac{9}{2} \alpha^{\text{lim}} 2f_{m'} \langle u_k(\mathbf{r}) u_m(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \\
& \quad - \frac{5}{9} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_k(\mathbf{r}) u_m(\mathbf{r}) \rangle .
\end{aligned} \tag{58}$$

The electronegativity can now be obtained directly by using

$$\chi = -\frac{1}{2}(\varepsilon_{m'}^{\dagger} + \varepsilon_k^{\dagger}) . \tag{59}$$

Adding Eqs (57) and (58) while recalling that the charge in these partially filled orbitals must add up to one gives

$$\begin{aligned}
\chi &= -\frac{1}{2}(\varepsilon_m' + \varepsilon_k) - \frac{1}{2}[f_{m'}]^{\text{GX/LSD-SI}} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle - \\
& \quad - \frac{1}{2}[(f_{k'} - 1) \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{\text{GX/LSD-SI}} - \\
& \quad - \frac{1}{2}(f_{m'}^{1/3} - 1) [6c\alpha^{\text{SI}} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle]^{\text{SI/LSD-SI/SIC}} - \\
& \quad - \frac{1}{2}(f_{k'}^{1/3} - 1) [6c\alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{\text{SI/LSD-SI/SIC}} + \\
& \quad + \frac{9}{2} \alpha^{\text{lim}} [B_1(f_{m'} - 1) + f_{m'}] \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} | u_m^2(\mathbf{r}) \rangle + \\
& \quad + \frac{9}{2} \alpha^{\text{lim}} (B_1 + 1)(f_{k'} - 1) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle - \\
& \quad - \frac{9}{2} \alpha^{\text{lim}} [B_2(f_{m'} - 1) + f_{m'}] \frac{2}{3} \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \times \\
& \quad \times \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m^2(\mathbf{r}) \rangle - \frac{9}{2} \alpha^{\text{lim}} (B_2 + 1)(f_{k'} - 1) \times \\
& \quad \times \frac{2}{3} \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle - \\
& \quad - \frac{9}{2} \alpha^{\text{lim}} f_{m'} \langle u_m^2(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k', m'=k}^s \{n_s^0 + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \\
& \quad - \frac{9}{5} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle -
\end{aligned}$$

$$\begin{aligned}
& - \frac{2}{3} c \alpha^{\text{lim}} (f_{k'} - 1) \langle u_k^2(\mathbf{r}) \rangle \frac{2}{3} \sum_{i \neq k', m'=k}^s \{n_s^0 + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \\
& - \frac{5}{9} \sum_{i \neq k', m'=k}^s \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) |u_k^2(\mathbf{r})\rangle, \quad (60)
\end{aligned}$$

where the $\langle u_k(\mathbf{r}) u_m(\mathbf{r}') | u_k(\mathbf{r}) u_m(\mathbf{r}') \rangle$ and all the $|u_k(\mathbf{r}) u_m(\mathbf{r}')\rangle$ terms add up exactly to zero because of the conservation of charge (Eq. (56)) in the χ -TS.

Any atom whose χ -TS involves partial electrons of parallel spins can only be an open shell atom such as boron or fluorine because the χ -TS is built according to Hund's rules. Therefore, the electronegativity expression (60) is only valid for open shell atoms which means that, in the unrelaxed approximation, the k^{th} and m^{th} orbitals are the same. In this case, Eq. (60) becomes

$$\begin{aligned}
\chi^{\text{op}} = & -\varepsilon_k + \left[-\frac{1}{2} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle \right]^{\text{SI/SIX/SIC}} - \\
& - \left\{ \frac{1}{2} (f_{k'}^{1/3} + f_m^{1/3}) - 1 \right\} \left[6c \alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle \right]^{\text{SI/LSD-SI/SIC}} - \\
& - \frac{2}{3} c \alpha^{\text{lim}} B_1 \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle + \\
& + \frac{2}{3} c \alpha^{\text{lim}} \frac{2}{3} B_2 \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle, \quad (61)
\end{aligned}$$

where the conservation of charge (Eq. (56)) has been used. It is important to note that *the only term that depends on the fractional occupation numbers of the k^{th} and m^{th} orbitals is the third term.* This electronegativity expression can be compared with the one derived previously from the definition of the *IP* and *EA* for open shell atoms, Eq. (52).

Therefore, *in all schemes, the negative of the average of the eigenvalues of the fractionally occupied HOAO and LUAO is a very good approximation to the electronegativity of the open shell atoms.* In addition, in the LSD GX and FE schemes, the negative of the eigenvalue of the fully occupied k^{th} orbital is the electronegativity of the open shell atoms, which is the same result that was derived earlier.^{12,20,21,23}

The Electronegativity Transition State Involving Partial Electrons of Opposite Spins

The k^{th} and m^{th} do not have the same spin. Therefore, neglecting orbital relaxation, the eigenvalue of the m^{th} orbital is

$$\varepsilon_{m'}^t = \langle u_{m'}(\mathbf{r}) | \mathbf{f}_r + \sum_{j=m'} f_j \langle u_j(\mathbf{r}') | u_j(\mathbf{r}') \rangle | u_{m'}(\mathbf{r}) \rangle +$$

$$\begin{aligned}
& + [-f_{m'} \langle u_{m'}(\mathbf{r}) u_{m'}(\mathbf{r}') | u_{m'}(\mathbf{r}) u_{m'}(\mathbf{r}') \rangle]^{SI/SIX/SIC} + \\
& + [6c\alpha^{SI} \langle u_{m'}(\mathbf{r}) | n_{m'}^{1/3}(\mathbf{r}) | u_{m'}(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} - \\
& - \frac{2}{3} c\alpha^{\text{lim}} \langle u_{m'}(\mathbf{r}) | \sum_{i=m'}^{s'} \{n_s^i(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-2/3} n_i(\mathbf{r}) - \\
& - \frac{2}{3} \sum_{i=m'}^{s'} \{n_s^i(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \{n_s^i(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) + \\
& + \{n_s^i(\mathbf{r}) + 2B_1 n_m(\mathbf{r})\} \{n_s^i(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} - \\
& - \frac{2}{3} B_2 \{n_s^i(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \{n_s^i(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} n_m(\mathbf{r}) | u_{m'}(\mathbf{r}) \rangle, \quad (62)
\end{aligned}$$

where

$$n_s^i(\mathbf{r}) = n_s^o(\mathbf{r}) + n_m(\mathbf{r}). \quad (63)$$

Using the same techniques as in the previous section gives

$$\begin{aligned}
\varepsilon_{m'}^i & = \varepsilon_{m'} + [f_{m'}]^{GX/LSD-SI} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle + \\
& + (f_{m'}^{1/3} - 1) [6c\alpha^{SI} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} - \\
& - \frac{2}{3} c\alpha^{\text{lim}} 2[B_1(f_{m'} - 1) + f_{m'}] \langle u_m^2(\mathbf{r}) | \{n_s^o(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} | u_m^2(\mathbf{r}) \rangle + \\
& + \frac{2}{3} c\alpha^{\text{lim}} 2[B_2(f_{m'} - 1) + f_{m'}] \frac{2}{3} \langle u_m^2(\mathbf{r}) | \{n_s^o(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \times \\
& \times \{n_s^o(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m^2(\mathbf{r}) \rangle + \frac{2}{3} c\alpha^{\text{lim}} 2f_{m'} \times \\
& \times \langle u_m^2(\mathbf{r}) | \frac{2}{3} \sum_{i \neq m'}^{s'} \{n_s^o(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \frac{5}{9} \sum_{i \neq m'}^{s'} \{n_s^o(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \times \\
& \times \{n_s^o(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle. \quad (64)
\end{aligned}$$

Similarly, the eigenvalue of the k' th orbital can be calculated, and expressed in terms of the eigenvalue of the fully occupied k th orbital ε_k and in terms of the ground state total electron density of the spin s electrons by using

$$n_s^i(\mathbf{r}) = n_s^o(\mathbf{r}) - n_k(\mathbf{r}) + n_{k'}(\mathbf{r}). \quad (65)$$

This gives

$$\begin{aligned}
\varepsilon_{k'}^i & = \varepsilon_k + [(f_{k'} - 1) \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{GX/LSD-SI} + \\
& + 9(f_{k'}^{1/3} - 1) [6c\alpha^{SI} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{SI/LSD-SI/SIC} -
\end{aligned}$$

$$\begin{aligned}
& - \frac{9}{2} c \alpha^{\text{lim}} 2(B_2 + 1)(f_{k'} - 1) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle + \\
& + \frac{9}{2} c \alpha^{\text{lim}} 2(B_2 + 1)(f_{k'} - 1) \frac{2}{3} \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \times \\
& \times \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle + \frac{9}{2} c \alpha^{\text{lim}} 2(f_{k'} - 1) \times \\
& \times \langle u_k^2(\mathbf{r}) | \frac{2}{3} \sum_{i \neq k'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) - \frac{5}{9} \sum_{i \neq k'} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} \times \\
& \times \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle . \tag{66}
\end{aligned}$$

The electronegativity can now be calculated using Eq. (59)

$$\begin{aligned}
\chi = & -\frac{1}{2}(\varepsilon_k + \varepsilon'_m) + [\frac{1}{4} \langle u_k(\mathbf{r}) u_k(\mathbf{r}') | | u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle]^{\text{GX/LSD-SI}} - \\
& - [2]^{\text{SI/SIX/SIC}} \frac{1}{4} \langle u_m(\mathbf{r}) u_m(\mathbf{r}') | | u_m(\mathbf{r}) u_m(\mathbf{r}') \rangle - \\
& - \frac{1}{2}(f_k^{1/3} - 1) [6c\alpha^{\text{SI}} \langle u_k(\mathbf{r}) | n_k^{1/3}(\mathbf{r}) | u_k(\mathbf{r}) \rangle]^{\text{SI/LSD-SI/SIC}} - \\
& - \frac{1}{2}(f_m^{1/3} - 1) [6c\alpha^{\text{SI}} \langle u_m(\mathbf{r}) | n_m^{1/3}(\mathbf{r}) | u_m(\mathbf{r}) \rangle]^{\text{SI/LSD-SI/SIC}} - \\
& - \frac{9}{4} c \alpha^{\text{lim}} \{ (1 + B_1) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-2/3} | u_k^2(\mathbf{r}) \rangle - \\
& - (1 - B_1) \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-2/3} | u_m^2(\mathbf{r}) \rangle \} + \\
& + \frac{9}{4} c \alpha^{\text{lim}} \frac{2}{3} \{ (1 + B_2) \langle u_k^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_k(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_k(\mathbf{r})\}^{-5/3} | u_k^2(\mathbf{r}) \rangle - \\
& - (1 - B_2) \langle u_m^2(\mathbf{r}) | \{n_s^0(\mathbf{r}) + B_1 n_m(\mathbf{r})\} \{n_s^0(\mathbf{r}) + B_2 n_m(\mathbf{r})\}^{-5/3} | u_m^2(\mathbf{r}) \rangle \} + \\
& + \frac{9}{4} c \alpha^{\text{lim}} \frac{2}{3} \{ \langle u_k^2(\mathbf{r}) | \sum_{i \neq k'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle - \\
& - \langle u_m^2(\mathbf{r}) | \sum_{i \neq m'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-5/3} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle \} - \\
& - \frac{9}{4} c \alpha^{\text{lim}} \frac{5}{9} \{ \langle u_k^2(\mathbf{r}) | \sum_{i \neq k'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} n_i(\mathbf{r}) | u_k^2(\mathbf{r}) \rangle - \\
& - \langle u_m^2(\mathbf{r}) | \sum_{i \neq m'} \{n_s^0(\mathbf{r}) + B_2 n_i(\mathbf{r})\}^{-8/3} \{n_s^0(\mathbf{r}) + B_1 n_i(\mathbf{r})\} n_i(\mathbf{r}) | u_m^2(\mathbf{r}) \rangle \} \tag{67}
\end{aligned}$$

which is very close to the electronegativity expression (51), the difference being the presence of the fourth and fifth terms in Eq. (67) instead of the *IP*-LSD-SI and *EA*-LSD-SI correction terms, respectively. If f_k and f_m are equal to $\frac{1}{2}$, the difference between these terms and the corresponding LSD-SI correction terms is negligible.

Therefore, this electronegativity expression is a very good approximation to the general electronegativity equation (51) which was derived rigorously from the unrelaxed IP and EA .

RESULTS

The GX-LSD-SI and GX-SIX results are not included, because they are worse than the ones presented, because these schemes have exchange potentials that violate the sum rule (ref.⁵).

Ionization Potentials

Table IV gives the IP 's of the helium to krypton atoms calculated using the FE, $X\alpha$ and GX schemes. The α 's used for the $X\alpha$ calculation are the spin-polarized α^{HF} (refs^{24,25}). In the GX scheme, the Free Electron Limit Fermi hole parameters were used².

The first column under each heading contains the TS eigenvalues, calculated by removing half an electron from the k^{th} orbital and subsequently doing an SCF calculation. The negative of the resulting eigenvalue of the remaining half an electron is the ϵ_k^{\downarrow} or IP .

The second column contains the corrected eigenvalue IP 's, IP_k^{corr} . After the SCF calculation of the neutral atom with all its orbitals at full occupancy, the resulting wavefunctions are used to evaluate the IP correction terms in Eq. (24). These are added to the eigenvalue. No SCF procedure is required other than the initial neutral atom calculation.

The FE and GX IP_k^{corr} are better than the corresponding TS IP 's when compared to experiment²⁶, while some $X\alpha$ TS IP 's are better than the corresponding IP_k^{corr} and some are not. For the transition metals, the GX IP_k^{corr} are the best.

The corrected eigenvalue method can also be used with the SI schemes. Table V gives the IP_k^{corr} for the helium to krypton atoms calculated using the SIC-FE scheme⁹ and the GX-SI scheme⁵ with the Free Electron Limit Fermi hole parameters². The SIC-FE IP_k^{corr} are slightly better than the GX-SI ones but overall they are close, and also close to experiment.

The deviation of each calculated IP , Tables IV and V, from the experimental value can be expressed as a percentage. These percentages can be averaged for all atoms to give the average percentage deviation from experiment. Table VI lists the average percentage deviations for the schemes discussed in this work for both the TS and corrected eigenvalue IP 's. These results indicate that the corrected eigenvalue IP method works very well for all DF schemes. Furthermore, numerically the difference between the best LSD and SI IP_k^{corr} are small hence, correcting the LSD schemes for self-interactions does not affect the trends of these IP 's.

TABLE IV

The TS and corrected eigenvalue IP 's of helium to krypton compared to the experimental ones. Energies in eV (1 eV = 96.4868 kJ mol⁻¹)

Atom	FE		X α		GX		Exp.
	$-\varepsilon_k^t$	IP_k^{corr}	$-\varepsilon_k^t$	IP_k^{corr}	$-\varepsilon_k^t$	IP_k^{corr}	
He	22.60	23.63	24.22	25.09	25.69	26.41	24.58
Li	5.12	5.02	5.67	5.53	5.85	5.67	5.39
Be	7.79	8.02	8.43	8.60	8.72	8.82	9.32
B	7.46	8.01	8.38	8.43	7.57	8.02	8.29
C	10.65	11.81	11.82	12.94	11.24	11.57	11.26
N	13.87	15.61	15.21	16.92	13.49	15.24	14.54
O	11.77	13.84	12.56	14.55	11.96	13.98	13.61
F	16.13	19.02	17.21	20.03	15.83	18.73	17.42
Ne	20.36	24.01	21.66	25.24	19.81	23.48	21.55
Na	4.93	4.87	5.25	5.16	5.63	5.48	5.13
Mg	6.57	6.76	6.92	7.08	7.35	7.43	7.64
Al	5.12	5.33	5.53	5.74	5.29	5.39	5.98
Si	7.39	7.87	7.94	8.41	7.80	7.77	8.14
P	9.63	10.35	10.31	11.01	10.00	10.18	11.00
S	8.74	9.70	9.26	10.15	9.03	9.87	10.35
Cl	11.66	12.86	12.24	13.47	11.59	12.77	13.01
Ar	14.43	15.89	15.20	16.64	14.22	15.68	15.75
K	4.08	4.04	4.31	4.26	4.62	4.52	4.33
Ca	5.19	5.33	5.43	5.55	5.78	5.94	6.11
Sc	5.46	5.60	5.68	5.80	6.10	6.17	6.56
Ti	5.64	5.77	5.86	5.96	6.33	6.38	6.83
V	6.71	5.91	6.96	6.09	7.07	6.56	6.74
Cr	7.00	7.31	7.25	7.55	7.38	7.59	6.76
Mn	6.08	6.16	6.28	6.34	6.87	6.88	7.43
Fe	6.73	6.92	6.95	7.13	7.43	7.52	7.89
Co	7.35	7.50	7.59	7.72	\cong 7.85	8.06	7.86
Ni	\cong 7.45	7.99	7.70	8.22	7.98	8.53	7.63
Cu	7.56	7.82	7.85	8.05	8.11	8.25	7.72
Zn	8.45	8.82	8.71	9.07	9.11	9.36	9.39
Ga	5.16	5.36	5.43	5.63	5.42	5.53	6.00
Ge	7.19	7.63	7.54	7.97	7.64	7.62	7.88
As	9.09	9.71	9.52	10.13	9.49	9.63	9.81
Se	8.25	9.02	8.55	9.31	8.56	9.26	9.75
Br	10.62	11.59	11.02	11.98	10.64	11.58	11.84
Kr	12.84	13.96	13.33	14.44	12.73	13.85	13.99

TABLE V

The corrected eigenvalue IP 's of helium to krypton calculated using the SIC-FE and GX-SI schemes, compared to the experimental ones. Energies in eV

Atom	SIC-FE	GX-SI	Exp.
He	24.98	24.98	24.58
Li	5.37	5.22	5.39
Be	8.49	8.32	9.32
B	8.79	7.72	8.29
C	12.63	11.18	11.26
N	16.46	14.75	14.54
O	14.53	13.43	13.61
F	19.71	18.05	17.42
Ne	24.69	22.69	21.55
Na	5.18	5.09	5.13
Mg	7.14	7.04	7.64
Al	5.73	5.09	5.98
Si	8.33	7.44	8.14
P	10.87	9.83	11.00
S	10.27	9.55	10.35
Cl	13.47	12.42	13.01
Ar	16.55	15.30	15.75
K	4.82	4.22	4.33
Ca	5.64	5.54	6.11
Sc	5.88	5.83	6.56
Ti	6.05	6.03	6.83
V	6.21	6.19	6.74
Cr	7.25	7.01	6.76
Mn	6.49	6.49	7.43
Fe	7.19	7.09	7.89
Co	7.74	7.60	7.86
Ni	8.21	8.04	7.63
Cu	7.77	7.56	7.72
Zn	9.03	8.83	9.39
Ga	5.74	5.22	6.00
Ge	8.05	7.30	7.88
As	10.19	9.30	9.81
Se	9.54	8.99	9.75
Br	12.14	11.27	11.84
Kr	14.56	13.53	13.99

Electronegativities

The electronegativities of free atoms can be derived by defining a neutral atom transition state that reflects the ground states of the positive and negative ions, and corresponds to a state half-way between the ground state configurations of the positive and negative ions. Although this is a mythical excited state of the neutral atom, it is mathematically valid within the framework of density-functional theory because the latter allows the use of non-integer occupation numbers of orbitals.^{3,12,13,22}

The spin-polarized electronegativity transition states of the helium to krypton atoms, are the ones defined by Manoli and Whitehead.²³

It is important to note that these χ -TS apply to calculations using the SI schemes. For the LSD schemes which have an orbital independent exchange potential, such as the LSD FE and $X\alpha$ schemes, removing a half-electron from the HOAO and placing it in the LDAO gives, for some open-shell atoms, a χ -TS which is exactly the same as the ground state electronic configuration. However, this is not true for self-interaction corrected schemes, because the exchange potential is always orbital dependent due, in part, to the presence of the exact, non-local self-interaction potential in the one-electron eigenvalue equation. Table VII gives the electronegativities of the helium to krypton atoms calculated using Eq. (59) with the FE, $X\alpha$, GX, SIC-FE and GX-SI schemes. Most of the $X\alpha$ χ 's are those calculated by Manoli and Whitehead.²³ These authors spin-averaged the eigenvalues with the same principal and azimuthal quantum numbers for some atoms such as the Noble gases. This is not done in this work. The χ 's of the lithium and boron atoms are equal to those calculated by Sen²⁷. The $X\alpha$ χ 's of the transition metals in this work are close but not equal to those calculated by Bartolotti et al.^{20,21} because these authors used different χ transition states. The GX, FE and $X\alpha$ schemes predict the electronegativities of aluminium and calcium lower than magnesium and potassium, respectively. These trends are incorrect. However, overall, the trends of the GX, FE and $X\alpha$ χ 's are the best when compared to electronegativities calculated by various other methods.²⁷⁻³³ The SIC-FE scheme gives χ 's that are significantly greater than those calculated using the other schemes while the GX-SI χ 's are close to the LSD ones.

TABLE VI

Average percentage deviation of the $-\varepsilon_k^I$ and IP_k^{corr} for the various schemes from the corresponding experimental IP 's for the helium to krypton atoms

Calculated quantities	FE	$X\alpha$	GX	SIC	GX-SI
$\Delta(-\varepsilon_k^I), \%$	10.4	6.5	6.7	—	—
$\Delta(IP_k^{\text{corr}}), \%$	7.1	6.7	5.0	5.4	6.3

TABLE VII

Electronegativities (in eV) of the helium to krypton atoms (Eq. (57)) with the FE, $X\alpha$, GX, GX-SI and SIC-FE schemes

Atom	FE	$X\alpha$	GX	GX-SI	SIC-FE
He	10.57	11.45	12.30	11.18	—
Li	2.15	2.54	2.76	2.42	4.97
Be	2.47	3.48	3.48	3.19	—
B	3.29	4.05	3.31	3.06	7.43
C	5.33	6.33	5.13	4.66	10.00
N	5.58	6.42	5.47	4.93	—
O	5.71	6.42	5.73	4.93	—
F	8.87	9.84	8.54	7.46	—
Ne	9.45	10.15	9.39	8.63	—
Na	2.10	2.32	2.68	2.37	4.66
Mg	2.56	2.81	3.05	2.78	5.18
Al	2.35	2.70	2.45	2.22	5.10
Si	3.91	4.39	3.85	3.50	7.05
P	4.30	4.76	4.34	3.95	7.65
S	4.74	5.18	4.87	4.40	8.28
Cl	6.92	7.50	6.82	6.26	10.80
Ar	6.64	7.07	6.73	6.30	9.81
K	1.75	1.92	2.23	1.97	3.86
Ca	1.50	1.74	1.72	1.80	—
Sc	2.77	2.90	3.21	2.75	4.64
Ti	2.86	3.01	3.31	2.86	4.86
V	2.95	3.11	3.42	2.97	5.06
Cr	3.04	3.20	3.52	3.07	5.28
Mn	3.40	3.56	3.84	3.26	5.52
Fe	3.50	3.67	\cong 3.9	3.38	5.73
Co	\cong 3.6	3.77	\cong 4.0	3.49	5.92
Ni	\cong 3.7	3.86	\cong 4.1	3.59	6.10
Cu	\cong 3.8	3.96	\cong 4.2	3.68	6.27
Zn	3.32	3.50	3.79	3.48	9.06
Ga	2.32	2.55	2.49	2.26	5.07
Ge	3.79	4.10	3.80	3.46	6.82
As	4.12	4.41	4.22	3.86	7.27
Se	4.51	4.80	4.70	4.27	7.80
Br	6.37	6.74	6.36	5.85	9.91
Kr	5.89	6.17	6.02	5.65	8.75

CONCLUSIONS

The corrected eigenvalue method of calculating IP 's for both the LSD and SI schemes predicts the best results when compared to those calculated using other IP schemes³⁴. This method eliminates the need for the unphysical transition state concept of removing half an electron to calculate the IP in the LSD schemes and, it compensates for the fact that the eigenvalues calculated using most of the SI schemes do not obey Koopmans' theorem. This method is also the most economical since it does not require a subsequent SCF calculation after the ground state one to obtain the IP of the atom.

Electronegativities cannot be uniquely defined nor measured directly³⁵ and hence, they can be calculated using a variety of methods^{20-23,27-33} which define the orbitals around the atom in the molecule in different ways, e.g. the atomic valence state. Hence, the concept of defining a χ -TS with non-integer occupation numbers can be exploited to derive electronegativities and this gives good results for the LSD schemes.

The Generalized Exchange scheme, with or without the self-interaction correction, predicts IP 's and χ 's which are as good as, if not better, than other LSD and SI schemes without the use of adjustable parameters such as the α^{HF} .

This research was supported by the NSERC(Canada).

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