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Generalized-exchange local-spin-density-functional theory: Self-interaction correction

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The local-spin-density (LSD) generalized-exchange (GX) theory is corrected for self-interaction by splitting the single-particle Fermi hole into pure-exchange and self-interaction holes. An analysis of these components shows that the non-self-interaction-corrected GX scheme overestimates the pure exchange while underestimating the self-interaction. This self-interaction-corrected scheme is called the GX-SI scheme. Using this method of correcting for self-interaction, two other approximate self-interaction-corrected (SIC) GX schemes can be derived in which (1) the GX-LSD-SI total exchange does not include the nonlocal, self-interaction potential and (2) the GX-SIX exchange is very similar to the exchange derived by Gopinathan [Phys. Rev. A **15**, 2135 (1977)]. Neither of these exchanges obeys the sum rule. The GX-SI scheme contains correction terms to the LSD GX which are smaller than the corresponding ones derived in the SIC of Perdew and Zunger [Phys. Rev. B **23**, 5048 (1981)]. This shows that the LSD-GX exchange is a better approximation to the true exchange of an inhomogeneous electron gas around an atom than the LSD free-electron gas exchange.

I. INTRODUCTION

The local-spin-density (LSD) $X\alpha$ exchange is[1] an approximate exchange for the inhomogeneous electron gas around a nucleus of charge Z. In the first paper,[1] the α parameter was defined using an *unspecified* LSD *Fermi hole,* averaged over all the nonlocal, orbital-pair exchange interactions.[1] This Fermi hole obeyed the boundary and normalization conditions of an *inhomogeneous* electron gas and gave rise to a theoretical α expression which is a function of the total number of electrons and is independent of the one-electron densities. The complete $X\alpha$ exchange is[1]

$$U^{X\alpha}(n_s(\mathbf{r})) = -9c\alpha^{\lim}(1+B_1/N_s)(1+B_2/N_s)^{-2/3}n_s^{1/3}(\mathbf{r}) , \quad (1)$$

where the $\alpha^{\lim}$, B_1, and B_2 values were determined by the specific shape of the Fermi hole and N_s is the number of electrons of spin s.

Four different Fermi holes were discussed;[1] the homogeneous Fermi hole,[2] the Gopinathan, Whitehead, and Bogdanovic Fermi hole,[3] modified Wigner Fermi hole,[4] and the free-electron-limit Fermi hole.[1] The larger the Fermi-hole radius the smaller α, and the exchange interaction.

The $X\alpha$ exchange was generalized by separating the total averaged Fermi hole, the average of all the Fermi holes around all the electrons, into single-particle Fermi holes around each electron.[1] This single-particle Fermi hole gives a local orbital-dependent exchange called the generalized exchange, LSD GX,

$$U_i^{\mathrm{GX}}(\mathbf{r}) = -9c\alpha^{\lim}[n_s(\mathbf{r})+B_1 n_i(\mathbf{r})] \times[n_s(\mathbf{r})+B_2 n_i(\mathbf{r})]^{-2/3} \quad (2)$$

of which the $X\alpha$ exchange is a special case, obtained either by calculating $\alpha^{\lim}$, B_1, and B_2 for the homogeneous Fermi-hole correlation factor, or by using the *classical* approximation

$$1/N_s \cong n_i(\mathbf{r})/n_s(\mathbf{r}) , \quad (3)$$

which is valid at large $|\mathbf{r}-\mathbf{r}'|$, the interelectronic separation. The homogeneous Fermi hole gives a constant α of 0.866 173, while approximation (3) gives α's that vary with the number of electrons.

The LSD-GX exchange *contains no adjustable parameters;* $\alpha^{\lim}$, B_1, and B_2 are rigorously calculated for a specific Fermi hole. Direct comparison of LSD-GX and $X\alpha$ exchange densities shows that the LSD GX has an α that is not only orbital dependent, but also varies at every point $\mathbf{r}$ in space; this is a more accurate description of the exchange interaction of an *inhomogeneous* electron gas.

II. SELF-INTERACTION

In Hartree-Fock (HF) theory, the total interelectronic interaction energy is

$$E_{ee}^{\mathrm{HF}} = \frac{1}{2}\sum_{i,j} f_i f_j \langle u_i(\mathbf{r})u_j(\mathbf{r}') \mid \mid u_i(\mathbf{r})u_j(\mathbf{r}')\rangle - \frac{1}{2}\sum_{i,j} f_i f_j \langle u_i(\mathbf{r})u_j(\mathbf{r}') \mid \mid u_i(\mathbf{r}')u_j(\mathbf{r})\rangle , \quad (4)$$

where $\mathbf{r}$ includes spin. The first term is the *Coulomb repulsion energy* and the second the *exchange energy.* When i equals j, the Coulomb and exchange terms cancel exactly; the interaction of an electron with itself is canceled. However, in LSD theory, the total interelectronic energy is

$$E_{ee}^{\mathrm{LSD}}=\tfrac{1}{2}\sum_{i,j} f_i f_j \langle u_i(\mathbf{r})u_j(\mathbf{r}')|\,|u_i(\mathbf{r})u_j(\mathbf{r}')\rangle + \tfrac{1}{2}\sum_i f_i \langle u_i(\mathbf{r})\,|\,U^{\mathrm{LSD}}i(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle \,, \tag{5}$$

where $U_i^{\mathrm{LSD}}(\mathbf{r})$ is a single-particle exchange density with a density-to-the-one-third dependence, $n^{1/3}(\mathbf{r})$. The self-interaction in the Coulomb term, i equals j, is not exactly canceled by the LSD exchange term because of the local nature of the exchange.[5-9]

Since the self-interaction energy can be calculated *exactly,* the exchange can be written as the sum of self-interaction and pure exchange

$$U_i^{\mathrm{LSD}}(\mathbf{r})=-f_i\langle u_i(\mathbf{r}')|\,|u_i(\mathbf{r}')\rangle+U_i^{\mathrm{exc}}(\mathbf{r}) \,. \tag{6}$$

This local exchange includes some nonlocal character through the self-interaction potential, and improves the description of an inhomogeneous gas in LSD theory.[5-9]

In this paper the local pure-exchange density $U_i^{\mathrm{exc}}(\mathbf{r})$ is derived by subtracting the self-interaction, calculated within the LSD and finite Fermi-hole radius approximations, from the total LSD single-particle exchange.

The single-particle Fermi-hole correlation factor is[1]

$$f_{ss}^{i}(\mathbf{r},\mathbf{r}')=n_i(\mathbf{r})/n_s(\mathbf{r})\{[n_i(\mathbf{r}')/n_s(\mathbf{r}')-1]h(\mathbf{r},\mathbf{r}') - n_i(\mathbf{r}')/n_s(\mathbf{r}')\} \,, \tag{7}$$

which *is exact* when the Fermi-hole function, or the pure-exchange correlation function $h(\mathbf{r},\mathbf{r}')$ is exact. When $h(\mathbf{r},\mathbf{r}')$ equals zero, the Fermi-hole correlation factor no longer includes exchange interactions, only self-interaction. The single-particle sum rule reduces to

$$\int n_i(\mathbf{r}')d\mathbf{r}'=1 \,. \tag{8}$$

the normalization condition of the ith one-electron density, and the total exchange becomes the self-interaction

$$U_i^{\mathrm{SI\text{-}X}}(\mathbf{r})=-\int n_i(\mathbf{r}')2/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}' \,. \tag{9}$$

Using the same approach on the *local,* single-particle Fermi-hole correlation factor, the normalization (8) becomes

$$n_i(\mathbf{r})\int_{v_{\mathrm{SI}}} d\mathbf{r}'=1 \,, \tag{10}$$

where v_{SI} is the volume within which the ith electron is present; it is assumed spherical in the LSD approximation. Equation (10) defines the *self-interaction hole,* centered at the point $\mathbf{r}$, within which the charge is assumed homogeneous. The Fermi-hole function $h(\mathbf{r},\mathbf{r}')$ defines the *pure-exchange hole.* The local normalization condition (10) can be integrated, and solved for the self-interaction hole radius r_{SI},

$$r_{\mathrm{SI}}=(3/4\pi)^{1/3}n_i^{-1/3}(\mathbf{r}) \,, \tag{11}$$

which is then used to evaluate the LSD-SI approximated potential from (9) which, upon integration, gives

$$U_i^{\mathrm{LSD\text{-}SI}}(\mathbf{r})=-9c\alpha^{\mathrm{SI}}n_i^{1/3}(\mathbf{r}) \,, \tag{12}$$

where c equals $(3/4\pi)^{1/3}$, and α^{SI} equals 0.866 173.[1]

Equation (12) is the LSD-SI approximated potential and *it is independent of the form of the total LSD exchange.* The α^{SI} of 0.866 173 equals the α^{lim} of the homogeneous Fermi-hole correlation factor[1] and *is constant for all systems.* This confirms the conclusions of Lindgren and Schwarz,[10] who decomposed the traditional $X\alpha$ exchange density parameter α^{HF} into a self-interaction parameter $\alpha_{\mathrm{SI}}^{\mathrm{HF}}$, and a pure-exchange parameter $\alpha_{\mathrm{IE}}^{\mathrm{HF}}$; $\alpha_{\mathrm{SI}}^{\mathrm{HF}}$ was decomposed into contributions from each shell. These parameters were *independent of the atomic number* and lay between 0.74 and 0.78. The average of these $\alpha_{\mathrm{SI}}^{\mathrm{HF}}$ values was approximately 0.77. The α^{SI} value of 0.866 173 obtained in the present work using the homogeneous self-interaction hole approximation, is near the empirically derived results of Lindgren and Schwarz,[10] and fits the observed trend.

Therefore the total self-interaction corrected exchange in the LSD theory is

$$U_i^{\mathrm{LSD}}(\mathbf{r})=-f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle + U_i^{\mathrm{LSD\text{-}X}}(\mathbf{r})-U_i^{\mathrm{LSD\text{-}SI}}(\mathbf{r}) \,, \tag{13}$$

where the last two terms are the pure exchange, $U_i^{\mathrm{exc}}(\mathbf{r})$ in (6), $U_i^{\mathrm{LSD\text{-}GX}}(\mathbf{r})$ is any total LSD exchange, and $U_i^{\mathrm{LSD\text{-}SI}}(\mathbf{r})$ is given by (12) *in every case.* Also if the $U_i^{\mathrm{LSD\text{-}GX}}(\mathbf{r})$ used in (13) contains correlation, the self-interaction correction will not affect it. Equations (12) and (13) define the LSD-SI theory.

III. SELF-INTERACTION CORRECTION IN THE LSD-GX THEORY

The LSD-GX exchange was derived[1] using a spherically symmetric, LSD-approximated single-particle Fermi-hole correlation factor satisfying the sum rule

$$-4\pi[n_s(\mathbf{r})-n_i(\mathbf{r})]\int_0^{r_F} h(r')r'^2dr' - 4\pi n_i(\mathbf{r})\int_0^{r_F} r'^2dr'=-1 \,. \tag{14}$$

The exchange in terms of the Fermi-hole correlation factor is

$$U_i^{X}(\mathbf{r})=-8\pi[n_s(\mathbf{r})-n_i(\mathbf{r})]\int_0^{r_F} h(r')r'dr' - 8\pi n_i(\mathbf{r})\int_0^{r_F} r'dr' \,. \tag{15}$$

Equations (14) and (15) form the basis of the LSD-GX theory. They define the exchange interaction of an electron gas around an atom within the LSD and the finite Fermi-hole radius approximations. The Fermi-hole radius is[1]

$$r_F=\{4\pi A_2[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]\}^{-1/3} \,, \tag{16}$$

with

$$A_2=\int_{u_F} h(u)u^2du, \quad u=r'/r_f \tag{17}$$

and

$$B_2=(1/3-A_2)/A_2 \,, \tag{18}$$

where u_F is the reduced Fermi-hole radius. The second term in (15) seems to be the LSD-SI-approximated potential;[1] however, *the limit of integration is the Fermi-hole radius r_F and not the radius of the self-interaction hole r_{SI}* defined by (11). r_{SI} was derived assuming the charge distribution within the self-interaction hole homogeneous. Even if r_F were obtained from the homogeneous Fermi hole[1] r_F would not equal r_{SI}. Thus, the LSD total exchange does not contain the correct self-interaction potential. The $X\alpha$ exchange is a special case of the LSD-GX exchange, and therefore the $X\alpha$ theory does not contain the correct self-interaction correction either.[5–17]

The amount of self-interaction in the LSD-GX exchange density is estimated by evaluating the second term in (15) using the Fermi-hole radius (16)

$$U_i^{\text{SI-GX}}(\mathbf{r})=-9c\alpha^{\text{lim}}/2A_1n_i(\mathbf{r})[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}\ , \tag{19}$$

where A_1 is[1]

$$A_1=\int_{u_F} h(u)u\,du,\quad u=r'/r_F \tag{20}$$

and α^{lim} is[1]

$$\alpha^{\text{lim}}=\tfrac{8}{9}(\pi^2/12)^{1/3}A_1A_2^{-2/3}\ , \tag{21}$$

with c equal to $(3/4\pi)^{1/3}$, B_2 defined by (18), and A_2 defined by (17). Using the homogeneous Fermi hole in the expression for the self-interaction (19) gives

$$U_i^{H\text{-SI}}(\mathbf{r})=-9c\alpha^{\text{lim}}n_i^{1/3}(\mathbf{r})[n_s(\mathbf{r})/n_i(\mathbf{r})]^{-2/3} \tag{22}$$

because B_2 equals zero, and α^{lim} equals 0.866 173, which equals α^{SI} of the previous section. The approximation (3) can be used in (22) to give

$$U_i^{H\text{-SI}}(\mathbf{r})=-9c\alpha^{\text{lim}}n_i^{1/3}(\mathbf{r})N_s^{-2/3}\ , \tag{23}$$

where α^{lim} of the homogeneous Fermi-hole correlation factor is equal to α^{SI}. This shows that *the* LSD-SI *part of the approximated potential of the* LSD-GX *exchange is underestimated by approximately* $N_s^{2/3}$. Consequently, when the LSD-SI scheme is applied to the LSD-GX exchange, the LSD-SI potential subtracts some pure exchange as well as self-interaction. Since the single-particle sum rule (14) consists of the pure-exchange hole, defined by $h(r')$, and the self-interaction hole, the radius of the total Fermi hole r_F *is the averaged radius of interaction of both these holes.* Comparing the self-interaction-hole radius (11) with the Fermi-hole radius (16) shows that r_F is smaller than r_{SI}, therefore the LSD self-interaction potential in the LSD-GX exchange density is too small. Conversely, the use of r_F must *overestimate the pure-exchange interaction to ensure that the sum rule (14) is satisfied.* Therefore, the LSD-SI scheme substracts the self-interaction portion of the LSD-GX exchange density as well as that *portion of the* LSD *pure-exchange density which is overestimated because r_F does not equal the correct radius of the pure-exchange hole.* When the r_{SI} calculated in II is used as the limit of integration of the self-interaction hole in the sum rule (14), a pure-exchange sum rule is obtained

$$-4\pi[n_s(\mathbf{r})-n_i(\mathbf{r})]\int_0^{r_{\text{ex}}} h(r')r'^2dr'=0\ , \tag{24}$$

where theoretically r_{ex} is the correct radius of the pure-exchange hole. Vaidehi and Gopinathan[18] derived a similar form of the pure-exchange sum rule, but they assumed r_{ex} equal to r_F, which is not correct within the LSD and finite radius approximations.

This shows that the total LSD-GX exchange can be evaluated in two parts: the pure-exchange interaction from the first term in (15) using the Fermi-hole radius (16) as an approximation to the true radius of the pure-exchange hole.

$$U_i^{\text{GX-exc}}(\mathbf{r})=-9c\alpha^{\text{lim}}[n_s(\mathbf{r})-n_i(\mathbf{r})]\times[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3} \tag{25}$$

and, the LSD-SI approximated potential from the second term in (15) using the radius of the self-interaction hole r_{SI} (11) to give

$$U_i^{\text{SI-GX}}(\mathbf{r})=-9c\alpha^{\text{SI}}n_i^{1/3}(\mathbf{r})\ , \tag{26}$$

the LSD-SI approximated potential (13). Adding (25) and (26) will give a total, self-interaction-corrected exchange that is completely local in nature; it will be called the GX-LSD-SI exchange density.

This exchange does not describe the inhomogeneous electron gas in an atom as well as the exchange obtained by substituting the original LSD-GX exchange density in the general form of the self-interaction-corrected exchange density of the LSD-SI scheme because the exact, nonlocal self-interaction potential is not explicitly included, and because the use of $\mathbf{r}_F$ instead of $\mathbf{r}_{\text{ex}}$ in (24) means that the GX-LSD-SI exchange does *not* obey the sum rule.

IV. SELF-INTERACTION-CORRECTED LSD-GX EXCHANGE DENSITIES

There are three self-interaction-corrected LSD-GX exchange densities: (1) The GX-LSD-SI exchange, the sum of (25) and (26),

$$U_i^{\text{GX-LSD-SI}}(\mathbf{r})=-9c\alpha^{\text{SI}}n_i^{1/3}(\mathbf{r})-9c\alpha^{\text{lim}}[n_s(\mathbf{r})-n_i(\mathbf{r})]\times[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}\ , \tag{27}$$

where α^{SI} is equal to 0.866 173. This contains no nonlocal character because the exact self-interaction potential is not used, but it is *computationally* easy. (2) The LSD-GX exchange can be used in the general form of the self-interaction-corrected exchange density derived from the LSD-SI theory in Sec. II,

$$U_i^{\text{GX-SI}}(\mathbf{r})=-f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle+9c\alpha^{\text{SI}}n_i^{1/3}(\mathbf{r})-9c\alpha^{\text{lim}}[n_s(\mathbf{r})+B_1n_i(\mathbf{r})]\times[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}\ . \tag{28}$$

This is the GX-SI exchange. Applying the SIC scheme of Perdew and Zunger[9] to the LSD-GX exchange gives exactly the GX-SI exchange, and confirms that the LSD-SI approximated potential (12) is independent of the form of the local LSD exchange. Specifically, it is independent of the Fermi-hole correlation factor used to determine α^{lim}, B_1, and B_2. (3) The completely local GX-LSD-SI exchange (30) can be corrected for self-interaction using the LSD-SI theory of Sec. II to ensure that the *exact* nonlocal self-interaction potential is included.

$$U_i^{\text{GX-SIX}}(\mathbf{r}) = -f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle - 9c\alpha^{\text{lim}}[n_s(\mathbf{r})-n_i(\mathbf{r})] \times [n_s(\mathbf{r})+B_2 n_i(\mathbf{r})]^{-2/3} . \quad (29)$$

The local self-interaction potential in (26) cancels the LSD-SI approximated potential in (13). This is the GX-SIX exchange. This exchange has the same form as the self-interaction-corrected local exchange *proposed* by Gopinathan,[8] the HFG theory. The HFG theory uses a variable parameter, a^{HF},[19,20] in the same way that the $X\alpha$ theory uses a variable α.[3,4,21]

The GX-SI exchange is the most rigorous. The difference between the GX-LSD-SI and GX-SIX exchange is that the LSD-SI approximated potential in the GX-LSD-SI theory has been replaced by the exact self-interaction potential in the GX-SIX theory. In both these self-interaction-corrected single-particle exchange densities, the pure exchange has been evaluated by integrating the LSD approximated pure-exchange hole $h(r')$ from zero to the radius r_F. To calculate the pure exchange within the finite radius approximation, the upper limit of integration should be the radius of the pure-exchange hole and not r_F. Therefore, the GX-SIX (and hence the HFG exchange) and GX-LSD-SI total exchange densities *do not obey the sum rule.*

V. SELF-INTERACTION CORRECTION AND THE FREE-ELECTRON GAS EXCHANGE DENSITY

An important limiting case of the self-interaction-corrected LSD-GX exchange is the free-electron gas limit. In the high electron density limit, the GX-SI exchange must reduce to the exact exchange derived by Dirac,[22] Gaspar,[33] and Kohn and Sham,[24] regardless of the scheme used to correct the LSD-GX exchange density for self-interaction.

The GX-SI exchange is given in Sec. IV as

$$U_i^{\text{GX-SI}}(\mathbf{r}) = -f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle + 9c\alpha^{\text{SI}} n_i^{1/3}(\mathbf{r}) - 9c\alpha^{\text{lim}}[n_s(\mathbf{r})+B_1 n_i(\mathbf{r})] \times [n_s(\mathbf{r})+B_2 n_i(\mathbf{r})]^{-2/3} \quad (30)$$

where α^{lim}, B_1, and B_2 are obtained from the free-electron-limit Fermi hole[1] and α^{SI} is 0.866 173. Rewriting,

$$U_i^{\text{GX-SI}}(\mathbf{r}) = -f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle - 9c\alpha^{\text{lim}} n_s^{1/3}(\mathbf{r}) \times \{[1+B_1 n_i(\mathbf{r})/n_s(\mathbf{r})][1+B_2 n_i(\mathbf{r})/n_s(\mathbf{r})]^{-2/3} - (\alpha^{\text{SI}}/\alpha^{\text{lim}})[n_i(\mathbf{r})/n_s(\mathbf{r})]^{1/3}\} . \quad (31)$$

At the free-electron limit, the high electron density limit, $n_i(\mathbf{r})/n_s(\mathbf{r})$ approaches zero, and hence (31) becomes

$$U_i^{\text{FE}}(\mathbf{r}) = -f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle - 9c\alpha^{\text{lim}} n_s^{1/3}(\mathbf{r}) . \quad (32)$$

The nonlocal self-interaction potential, the first term in (32), is negligible compared to the total Coulomb repulsion, and hence the exchange in the high electron density limit is

$$U^{\text{FE}}(n_s(\mathbf{r})) = -9c\alpha^{\text{lim}} n_s^{1/3}(\mathbf{r}) , \quad (33)$$

the exact exchange potential of the free-electron gas. Therefore, the GX-SI exchange reduces to the correct free-electron gas exchange as the total electron density gets large. The only self-interaction correction present is than in (33). Therefore, the free-electron gas exchange will underestimate the exchange of an inhomogeneous electron gas because the self-interaction potential is underestimated.

Perdew and Zunger[9] applied the SIC theory to the exact free-electron gas exchange, which they used to approximate the exchange for the inhomogeneous electron gas, assuming that the self-interaction-corrected exchange would account in part for the inhomogeneity of the electron gas; α was set equal to $\frac{2}{3}$. The self-interaction-corrected total exchange from their SIC theory applied to the free-electron gas exchange density is

$$U_i^{\text{SIC-}X}(\mathbf{r}) = -9c(\tfrac{2}{3}) n_s^{1/3}(\mathbf{r}) - f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle + 9c(\tfrac{2}{3}) n_i^{1/3}(\mathbf{r}) . \quad (34)$$

The last term in (34) is the SIC LSD-SI approximated potential which does *not* have the α^{SI} derived in Sec. II. This discrepancy is caused by the fact that the LSD-GX exchange uses a *finite Fermi-hole radius* approximation which obeys the correct normalization conditions of an electron gas, while the free-electron gas exchange has been derived from *homogeneous* electron gas considerations with an infinite Fermi hole radius. This exchange reduces to the correct free-electron gas exchange at the high electron density limit.

The Perdew and Zunger approach to solving the inhomogeneous electron gas problem is from homogeneous electron gas considerations, while the exchange density derived in the present work attempts to describe the inhomogeneous electron gas in the LSD approximation using the finite Fermi-hole radius approximation.

The difference between these two approaches can be investigated further by estimating the magnitude of the total self-interaction correction in both cases. Gadre, Bartolotti and Handy[22] have shown that the total Coulomb repulsion energy of an electron density $n(\mathbf{r})$, *obtained from the free-electron gas Thomas-Fermi theory,* satisfies the inequality

$$\tfrac{1}{2}\sum_{i,j} f_i f_j \langle u_i(r)u_j(\mathbf{r}')\|u_i(\mathbf{r})u_j(\mathbf{r}')\rangle \leq 2.184N^{2/3}\int n^{4/3}(\mathbf{r})d\mathbf{r}\ , \tag{35}$$

where N is the total number of electrons and units are rydbergs. For a singly occupied orbital density, this inequality becomes

$$\tfrac{1}{2}f_i f_i \langle u_i(\mathbf{r})u_i(\mathbf{r}')\|u_i(\mathbf{r})u_i(\mathbf{r}')\rangle \leq 2.184\int n_i^{4/3}(\mathbf{r})d\mathbf{r}\ . \tag{36}$$

The LSD-SI approximated energy obtained from the last term of (34) is

$$(9c/2)(\tfrac{2}{3})\int n_i^{4/3}(\mathbf{r})d\mathbf{r}=1.8610\int n_i^{4/3}(\mathbf{r})d\mathbf{r} \tag{37}$$

and since (36) is generally close to an equality,[9] the self-interaction corrected exchange (34) becomes

$$U_i^{\text{SIC-X}}(\mathbf{r})=-9c(\tfrac{2}{3})n_s^{1/3}(\mathbf{r})-0.646n_i^{1/3}(\mathbf{r})\ . \tag{38}$$

Therefore, the self-interaction-correction terms, local and nonlocal, in (34) make the total energy more negative, which implies that the use of the non-self-interaction-corrected free-electron gas exchange gives a total energy which is too high for the inhomogeneous electron gas. This is not unexpected within the present theoretical framework because the α^{HF} values of the atoms are greater than $\frac{2}{3}$.[23]

The LSD-SI approximated potential in the LSD-GX exchange, obtained from the LSD-SI theory of II gives the total self-interaction energy

$$(9c/2)(0.866\,173)\int n_i^{4/3}(\mathbf{r})d\mathbf{r} =2.4180\int n_i^{4/3}(\mathbf{r})d\mathbf{r}\ . \tag{39}$$

Using (39) and replacing the nonlocal self-interaction energy by (36), the total self-interaction-corrected GX-SI exchange becomes

$$U_i^{\text{GX}-\text{SI}}(\mathbf{r})=U^{\text{GX}}(\mathbf{r})+0.468n_i^{1/3}(\mathbf{r})\ . \tag{40}$$

The LSD-GX *exchange gives a total energy which is too negative,*[1] and the self-interaction correction is positive to compensate because the LSD approximated sum rule, which uses the finite Fermi-hole radius approximation to describe the inhomogeneous electron gas, overestimates the pure-exchange interaction because the Fermi-hole radius r_F is not equal to the pure-exchange hole radius. The self-interaction correction is smaller when α^{SI} equals 0.866 173 than when α^{SI} equals $\frac{2}{3}$. Therefore the LSD exchange derived using the finite Fermi-hole radius approximation is closer to the correct exchange density.

The LSD-GX exchange is a better theoretical approximation to the correct exchange of the electron gas around a nucleus of charge Z than the homogeneous free-electron gas exchange.

VI. CONCLUSION

The LSD-SI approximated potential is subtracted from the total, pure exchange plus self-interaction LSD exchange to give the pure-exchange LSD exchange, which is then added to the exact, nonlocal self-interaction potential to give the self-interaction-corrected LSD exchange. This is the LSD-SI theory.

This self-interaction-correction scheme was applied to LSD-GX exchange to give a self-interaction-corrected exchange, called the GX-SI exchange, which is rigorous within the LSD and finite Fermi-hole radius approximations.

Separating the Fermi hole into a self-interaction and a pure-exchange hole, each with its own radius of interaction, gives a self-interaction-corrected LSD exchange which is *completely local in nature:* the exact, nonlocal self-interaction potential is absent. This is the GX-LSD-SI exchange.

This was used as the approximate exchange density in the LSD-SI theory of Sec. II. The resulting total exchange density has the same local pure-exchange term as the GX-LSD-SI exchange density, but has the exact, nonlocal self-interaction potential. This is the GX-SIX exchange density which is almost the same as the HFG exchange of Gopinathan.[8,19,20]

The GX-LSD-SI, GX-SIX, and HFG exchange densities are not expected to describe the interactions of an inhomogeneous electron gas very well because using r_f as the approximate radius of the pure-exchange hole violates the sum rule.

At the free-electron limit, it was found that applying the SIC theory[9] to the free-electron exchange gave a local self-interaction potential not equal to the LSD-SI approximated potential derived from the LSD-GX exchange because the free-electron gas exchange does not use the finite Fermi-hole radius approximation.

Comparison of the GX-SI and other self-interaction-corrected free-electron exchange densities showed the former to better approximate the correct exchange of the inhomogeneous electron gas in an atom. This comparison showed the the non-self-interaction-corrected LSD-GX exchange gave total energies *below* the correct ones, while the non-self-interaction-corrected free-electron exchange gives total energies *above* the correct ones because, even though both the LSD-GX and free-electron gas exchange densities underestimate the local self-interaction correction, the LSD-GX exchange density overestimates the pure-exchange interaction.[1]

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