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Extension of the local-spin-density exchange-correlation approximation to multiplet states

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Summary. We investigate a simple generalization of the local-spin-density exchange-correlation approximation of density-functional theory from single to multi-determinantal states. The method is explicitly spin independent and trivially preserves multiplet spin degeneracies. Tests on multiplet splittings in a variety of low-lying configurations of first-row atoms and ions are presented.

Key words: Density-functional theory – Multiplets

1. Introduction

The local-spin-density (LSD) approximation for the exchange-correlation energy of multi-electron systems has found wide application in many areas of theoretical physics and chemistry (see [1] and references therein). Ziegler et al. [2] have pointed out, however, that the LSD approximation is justified in single determinantal states only, and straightforward application to determinantal superpositions is not permitted. These authors have nevertheless shown that the energies of multi-determinantal states may be expressed in many cases as linear combinations of single-determinantal LSD energies.

In this work, we discuss an alternative approach to multiplet energy calculations based on a simple extension of the original LSD philosophy. All we require is a transformation from local spin-densities as independent variables to *total* density and local *pair* density instead. Explicit spin dependence is thereby eliminated, and exchange-correlation functionals which properly reproduce multiplet spin degeneracies are derived. The use of spinless local pair density in *correlation* functionals for open-shell systems has been espoused previously [3], but here we consider its application to open-shell *exchange* as well.

2. Basic theory

The LSD exchange-correlation energy depends, as the name implies, on the local spin-densities ρ_α and ρ_β as independent variables. Equivalently, the total electronic density ρ and the spin polarization factor ζ defined by

$$\zeta = (\rho_\alpha - \rho_\beta)/\rho \tag{1}$$

may be used as independent variables instead (as is often done in the density-functional literature). Numerous alternative independent variable pairs are, of course, also conceivable.

We shall see soon that the total density ρ and the local *pair* density are particularly suitable independent variables in multi-determinantal situations. Letting $\boldsymbol{x}_i$ represent space and spin coordinates $(\boldsymbol{r}_i, \sigma_i)$ of particle i and adopting the two-body density matrix normalization of McWeeny [4], we define the spinless "local pair" density $P_2(\boldsymbol{r})$ as follows:

$$P_2(\boldsymbol{r}) = N(N-1) \int |\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_N)|^2 \, \mathrm{d}\sigma_1 \, \mathrm{d}\sigma_2 \, \mathrm{d}\boldsymbol{x}_3 \cdots \mathrm{d}\boldsymbol{x}_N \Bigg|_{\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}}, \tag{2}$$

which is nothing more than the spinless two-body probability density $\Pi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ of [4] evaluated at $\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}$. We propose that the LSD exchange-correlation energy be viewed hereafter as a functional of ρ and P_2. For a single-determinantal state, P_2 is related to spin densities ρ_α and ρ_β and the spin polarization factor ζ by

$$P_2 = 2\rho_\alpha \rho_\beta = \tfrac{1}{2}\rho^2(1 - \zeta^2) \tag{3}$$

and through these relations the transformation from spin density or "ρ–ζ" functionals to "ρ–P_2" functionals is established.

For example, the LSD approximation for exchange only is, for a single Slater determinant [5],

$$E_{\mathrm{X}}^{\mathrm{LSD}} = -C_{\mathrm{X}} \int (\rho_\alpha^{4/3} + \rho_\beta^{4/3}) \, \mathrm{d}^3\boldsymbol{r}, \quad C_{\mathrm{X}} = \tfrac{3}{2}\left(\tfrac{3}{4\pi}\right)^{1/3} \tag{4}$$

in terms of independent variables ρ_α and ρ_β. In terms of ρ and ζ we have the equivalent formula

$$E_{\mathrm{X}}^{\mathrm{LSD}} = -2^{-4/3} C_{\mathrm{X}} \int \rho^{4/3} F(\zeta) \, \mathrm{d}^3\boldsymbol{r}, \tag{5}$$

where

$$F(\zeta) = (1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}. \tag{6}$$

Inverting Eq. (3) to obtain ζ as a function of ρ and P_2:

$$\zeta^2 = 1 - 2P_2/\rho^2, \tag{7}$$

we obtain the dependence of E_{X} on the density ρ and the local pair density P_2.

These complementary viewpoints are equally efficacious in single-determinantal states. Straightforward application of the LSD approximation to multiplet states, however, results in artificial and unphysical splitting of spin-degenerate levels. Even in the simplest conceivable case of the triplet spin states of a two-electron two-orbital configuration, significant energy splittings arise from different spin densities in the triplet spin components. Moreover, the singlet state is, in the LSD approximation, incorrectly *degenerate* with the $M_{\mathrm{S}} = 0$ triplet component [6, 7].

Alternatively, the total density ρ and the local pair density P_2 are equivalent in all components of a spin multiplet, and an obvious generalization of the LSD approximation thus suggests itself. Treat the LSD approximation as a functional of the *multiplet* ρ and the *multiplet* P_2, instead of ρ_α and ρ_β. Substitute ρ and P_2 into Eqs. (5)–(7), for example, in the case of pure exchange. We shall call this modification of the LSD philosophy the "local density/pair density" (LDPD) approximation.

In the LDPD scheme, we encounter an interesting mathematical complication. In single-determinantal states, the range of the local pair density P_2 is given by

$$0 \leqslant P_2 \leqslant \rho^2/2 \tag{8}$$

corresponding to the following range of the spin polarization factor ζ

$$1 \geqslant \zeta^2 \geqslant 0. \tag{9}$$

The upper limit $P_2 = \rho^2/2$ is not applicable, however, in *multi*-determinantal states (an elementary example is presented in the following section) and the possibility of negative ζ^2 and formally imaginary ζ thus arises. Exchange-correlation functionals are nevertheless *even* functions of ζ (i.e. functions of ζ^2, as demanded by spin symmetry) and are therefore *real* under all conditions. Considering again the exchange-only example, the following representation of $F(\zeta)$ of Eq. (6) is easily derived for the imaginary-ζ case:

$$F(\zeta) = 2(1 + \eta^2)^{2/3} \cos(\tfrac{4}{3} \arctan \eta) \tag{10a}$$

when

$$\zeta = \pm i\eta. \tag{10b}$$

The imaginary-ζ behaviour of more complicated functionals, such as the Vosko et al. [8] or the Perdew and Wang [9] correlation functionals, can be similarly represented with relatively little effort. We shall assume at the outset that LSD exchange-correlation functionals continue to hold their physical significance in this extrapolated regime.

We emphasize that in multiplet states the ζ variable, as employed here, does *not* correspond to the physical M_S values of the multiplet spin components. In order to extend the applicability of existing ρ–ζ functionals in the literature to multiplet states, we have replaced the original definition of Eq. (1) for ζ by Eq. (7).

3. An elementary example

To illustrate the LDPD approach, consider the simple special case of two-electron two-orbital singlet and triplet multiplets given by

$$\Psi_{\substack{\text{sing}\\ \text{trip}}} = 2^{-1/2}(\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2))\,\chi_{\substack{\text{sing}\\ \text{trip}}} \tag{11}$$

with orthonormal one-electron spatial orbitals ϕ_a and ϕ_b and well-known two-electron total spin states χ_{sing} and χ_{trip}. We easily deduce the density ρ and the local pair density P_2 for each of these states as follows:

$$\begin{aligned} \rho &= \phi_a^2 + \phi_b^2, \qquad P_2 = 4\phi_a^2\phi_b^2 \quad (\textit{singlet}) \\ \rho &= \phi_a^2 + \phi_b^2, \qquad P_2 = 0 \quad (\textit{triplet}) \end{aligned} \tag{12}$$

which we now take, through Eq. (7), as arguments of our LDPD exchange-correlation energy. Even in this simplest possible case, the "normal" upper P_2 limit of Eq. (8) is easily exceeded. At points in space where $\phi_a(r) = \phi_b(r)$, for instance, singlet P_2 has value ρ^2, and ζ is formally imaginary.

Table 1. Singlet-triplet splittings in He (eV)

	Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
1*s*2*s*	1.02	0.72	0.87	0.80
1*s*2*p*	0.41	0.43	0.33	0.25

This simple two-electron theory has been applied to the 1*s*2*s* and 1*s*2*p* configurations of the atom He. Using numerical, spin-unpolarized LSD orbitals for both singlet and triplet states (spherically averaged in the case of 2*p*), we obtain the singlet-triplet splittings of Table 1. Column "local XC" corresponds to LDPD implementation of Eq. (5) for exchange and the local correlation functional of Perdew and Wang [9]. The other columns are discussed below. Despite the simplicity of LDPD theory, agreement between experiment [10] and our "local XC" results is reasonably good. More complex multiplet splittings are considered in the following section.

4. First-row atoms and ions

We have developed a general procedure to obtain spherically averaged local pair densities P_2 in a wide variety of atomic multiplets. Its derivation is deferred to the Appendix, while a brief outline is given below.

The procedure exploits the extensive tabulations by Slater of atomic Hartree-Fock multiplet energies in [11]. There, the Coulomb energies of atomic multiplets are expressed as linear combinations of radial integrals denoted $\mathrm{F}^k(a,b)$ and $\mathrm{G}^k(a,b)$, where a and b are orbital labels. On page 343 of Vol. 1, for example, the energies of $s^m p^n$ multiplets are so tabulated. Corresponding to each of the F^k and G^k *integrals*, we define in the present work the *functions*

$$\mathfrak{F}^k(a,b;r) = \mathfrak{G}^k(a,b;r) = \frac{2k+1}{8\pi^2} R_a^2(r) R_b^2(r), \tag{13}$$

where $R_a(r)$ and $R_b(r)$ are the usual atomic radial functions. The spherically averaged local P_2 of a multiplet is then given by

$$P_2 = \sum_{abk} f_k(a,b)\, \mathfrak{F}^k(a,b;r) + \sum_{abk} g_k(a,b)\, \mathfrak{G}^k(a,b;r), \tag{14}$$

where the coefficients f_k and g_k are the same as those tabulated in [11].

We have used these spherically symmetrized local pair densities and spherically symmetrized total densities ρ to calculate multiplet splittings in all first-row ground and singly-excited-state $2s^m 2p^n$ configurations of neutral, singly, and doubly ionized atoms. The results are presented in Tables 2–9. Orbitals were obtained by numerical, spin-restricted Kohn-Sham calculations (in the LSD approximation, with the correlation functional of [9]), and "exact" exchange splittings were obtained by numerical evaluation of F^k and G^k integrals using the same orbitals. By "exact" exchange, we mean essentially Hartree-Fock theory, except that the orbitals of the present work are Kohn-Sham rather than Hartree-Fock orbitals.

Table 2. $2s^1 2p^1$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
Be	^1P–^3P	3.61	1.81	2.70	2.55
B^+	^1P–^3P	5.63	3.15	4.58	4.47
C^{2+}	^1P–^3P	7.44	4.46	6.31	6.20

Table 3. $2s^1 2p^2$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
B	^2P–^4P	7.29	3.50	6.09	5.42
	^2D–^4P	3.63	2.52	2.77	2.36
	^2S–^4P	5.44	4.21	4.00	4.31
C^+	^2P–^4P	10.22	5.20	8.92	8.38
	^2D–^4P	5.23	3.91	4.26	3.95
	^2S–^4P	7.97	6.64	6.33	6.63
N^{2+}	^2P–^4P	12.91	6.86	11.57	10.99
	^2D–^4P	6.73	5.29	5.70	5.42
	^2S–^4P	10.36	9.04	8.61	9.14

Table 4. $2s^2 2p^2$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
C	^1D–^3P	1.50	1.38	1.18	1.26
	^1S–^3P	3.75	3.31	2.95	2.68
N^+	^1D–^3P	2.15	2.06	1.78	1.89
	^1S–^3P	5.37	4.96	4.45	4.04
O^{2+}	^1D–^3P	2.76	2.72	2.36	2.49
	^1S–^3P	6.90	6.55	5.90	5.33

We find, unfortunately, that the LDPD approximation for exchange-correlation together ("local XC" in the tables) performs unreliably, giving reasonably good results in configurations $2s^2 2p^n$ but very poor results in $2s^1 2p^n$. Our splittings are similar to those of Gunnarsson and Jones [7] obtained by the method of Ziegler et al [2], and reflect the same electron-hole asymmetry in conjugate configurations reported by them. Electron-hole asymmetry is apparently a fundamental weakness of density-functional approximations whether implemented by the multiplets scheme of Ziegler et al [2] or by the present scheme.

Table 5. $2s^12p^3$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
C	^{3}S–^{5}S	12.13	5.42	10.64	8.93
	^{3}D–^{5}S	5.31	3.74	4.26	3.76
	^{1}D–^{5}S	11.37	6.25	9.70	7.95
	^{3}P–^{5}S	6.83	5.16	5.44	5.15
	^{1}P–^{5}S	12.89	7.55	10.88	10.68
N^+	^{3}S–^{5}S	15.95	7.39	14.38	13.39
	^{3}D–^{5}S	7.20	5.32	6.05	5.59
	^{1}D–^{5}S	15.17	8.72	13.38	12.03
	^{3}P–^{5}S	9.33	7.39	7.82	7.69
	^{1}P–^{5}S	17.31	10.61	15.14	14.83
O^{2+}	^{3}S–^{5}S	19.53	9.33	17.92	16.96
	^{3}D–^{5}S	8.99	6.89	7.79	7.41
	^{1}D–^{5}S	18.75	11.16	16.89	15.71
	^{3}P–^{5}S	11.73	9.60	10.13	10.18
	^{1}P–^{5}S	21.49	13.65	19.22	18.62

Table 6. $2s^22p^3$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
N	^{2}D–^{4}S	2.72	2.35	2.27	2.38
	^{2}P–^{4}S	4.54	3.86	3.80	3.58
O^+	^{2}D–^{4}S	3.69	3.27	3.19	3.32
	^{2}P–^{4}S	6.15	5.37	5.32	5.02
F^{2+}	^{2}D–^{4}S	4.61	4.16	4.07	4.23
	^{2}P–^{4}S	7.68	6.83	6.80	6.39

Table 7. $2s^12p^4$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
N	^{2}P–^{4}P	10.85	4.15	10.01	
	^{2}D–^{4}P	5.45	2.99	4.85	
	^{2}S–^{4}P	8.19	5.26	7.15	
O^+	^{2}P–^{4}P	13.68	5.32	12.82	11.49
	^{2}D–^{4}P	7.01	3.96	6.38	5.71
	^{2}S–^{4}P	10.68	7.05	9.57	9.39
F^{2+}	^{2}P–^{4}P	16.36	6.48	15.49	14.21
	^{2}D–^{4}P	8.50	4.92	7.86	7.21
	^{2}S–^{4}P	13.08	8.81	11.93	11.92

Table 8. $2s^2 2p^4$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
O	^{1}D–^{3}P	2.13	1.67	1.86	1.96
	^{1}S–^{3}P	5.31	4.10	4.65	4.18
F$^+$	^{1}D–^{3}P	2.77	2.20	2.48	2.57
	^{1}S–^{3}P	6.91	5.41	6.19	5.55
Ne^{2+}	^{1}D–^{3}P	3.38	2.72	3.07	3.16
	^{1}S–^{3}P	8.45	6.68	7.68	6.87

Table 9. $2s^1 2p^5$ multiplet splittings (eV)

		Exact exchange	Local XC	Exact exchange + GGA91 correlation	Expt.
O	^{1}P–^{3}P	8.39	2.91	7.89	7.88
F$^+$	^{1}P–^{3}P	10.26	3.59	9.76	9.26
Ne^{2+}	^{1}P–^{3}P	12.04	4.26	11.54	10.52

LDPD theory remains useful, however, as a tool for evaluating *correlation only* corrections to exact-exchange multiplet splittings. It is clearly demonstrated by the "exact exchange" data in our tables that pure, exact exchange overestimates multiplet splittings due to lack of dynamical electron correlation. Consider, on the other hand, the "exact exchange + GGA91 correlation" data obtained by adding LDPD dynamical correlation to the exact-exchange results. We utilize the best correlation functional currently available: the functional of Perdew and Wang [9, 12, 13] (sometimes called GGA91) including an inhomogeneity term [12, 13] depending on the total density *gradient* $\nabla\rho$. The "exact exchange + GGA91 correlation" splittings agree reasonably well with experiment [10], with a maximum deviation of 1.75 eV, and an average absolute deviation of only 0.46 eV. A tendency to overestimate the multiplet splittings remains, which future correlation functionals may, perhaps, reduce. The "exact exchange" splittings without correlation correction suffer significantly larger deviations from experiment of 3.42 eV maximum and 1.40 eV on average.

5. Conclusions

We have examined a straightforward extension of the local-spin-density exchange-correlation approximation from single to multi-determinantal reference states. A transformation of independent variables from local spin-densities to *total* density and local *pair* density is all we require. Computation of multiplet splittings in first-row atoms and ions confirms the finding of Gunnarsson and Jones [7] that density-functional approximations fail to reproduce electron-hole symmetry in conjugate configurations. If exchange is treated exactly, however, the present method furnishes useful dynamical correlation corrections which largely rectify the tendency of Hartree-Fock theory to overestimate multiplet splittings. Generalization of the method to molecular systems, and removal of spherical averaging in atomic systems, will be undertaken in future work.

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Appendix

The total interelectronic repulsion energy of a multi-electron system is given by

$$\mathrm{E}^{(2)}_{\mathrm{Coul}} = \frac{1}{2}\int\int \Pi(\boldsymbol{r}_1,\boldsymbol{r}_2)\frac{1}{r_{12}}\,d^3\boldsymbol{r}_1\,d^3\boldsymbol{r}_2. \tag{A1}$$

where $\Pi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the spinless two-body probability density normalized as in [4] and Eq. (2). As discussed at length in [11], this energy can be written in the form

$$\mathrm{E}^{(2)}_{\mathrm{Coul}} = \sum_{abk} f_k(a,b)\,\mathrm{F}^k(a,b) + \sum_{abk} g_k(a,b)\,\mathrm{G}^k(a,b). \tag{A2}$$

where f_k and g_k are coefficients tabulated for a wide variety of atomic multiplets in [11], and F^k and G^k are the following radial integrals:

$$\mathrm{F}^k(a,b) = \int_0^\infty\int_0^\infty R_a^*(1)R_b^*(2)R_a(1)R_b(2)\frac{r_<^k}{r_>^{k+1}}r_1^2r_2^2\,\mathrm{d}r_1\,\mathrm{d}r_2, \tag{A3}$$

$$\mathrm{G}^k(a,b) = \int_0^\infty\int_0^\infty R_a^*(1)R_b^*(2)R_b(1)R_a(2)\frac{r_<^k}{r_>^{k+1}}r_1^2r_2^2\,\mathrm{d}r_1\,\mathrm{d}r_2. \tag{A4}$$

In these integrals, a and b are orbital labels, $R(r)$ is the usual radial part of an atomic orbital, and $r_<$ ($r_>$) denotes the lesser (greater) of the two radii r_1 and r_2. The derivation of Eqs. (A2)–(A4) is based on the well-known spherical harmonic expansion

$$r_{12}^{-1} = \sum_{k=0}^{\infty}\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}\sum_{m=-k}^{+k}Y_{km}^*(\Omega_1)\,Y_{km}(\Omega_2). \tag{A5}$$

The f_k and g_k coefficients contain the results of all the *angular* integrations over Ω_1 and Ω_2 implied in Eq. (A1). Therefore, let us write

$$\int \mathrm{d}\Omega_1 \int \mathrm{d}\Omega_2\, r_{12}^{-1}\,\Pi(\boldsymbol{r}_1,\boldsymbol{r}_2) = 2\sum_{abk} f_k(a,b)\,R_a^*(1)R_b^*(2)R_a(1)R_b(2)\frac{r_<^k}{r_>^{k+1}}$$
$$+\,2\sum_{abk} g_k(a,b)\,R_a^*(1)R_b^*(2)R_b(1)R_a(2)\frac{r_<^k}{r_>^{k+1}} \tag{A6}$$

an expression we will use below.

The spherical average of the local pair density $P_2(r_1)$ is given by

$$\begin{aligned} P_2(r_1) &= \frac{1}{4\pi}\int d\Omega_1\, \Pi(\boldsymbol{r}_1,\boldsymbol{r}_1) \\ &= \frac{1}{4\pi}\int d\Omega_1 \int d^3r_2\, \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\Pi(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ &= \frac{1}{4\pi}\int dr_2\, r_2^2 \int d\Omega_1 \int d\Omega_2\, \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\Pi(\boldsymbol{r}_1,\boldsymbol{r}_2). \end{aligned} \tag{A7}$$

Recognizing that the delta function $\delta(\boldsymbol{r}_1-\boldsymbol{r}_2)$ has a spherical harmonic expansion analogous to Eq. (A5) for r_{12}^{-1}:

$$\delta(\boldsymbol{r}_1-\boldsymbol{r}_2) = \frac{\delta(r_1-r_2)}{r_1^2}\sum_{k=0}^{\infty}\sum_{m=-k}^{+k} Y_{km}^*(\Omega_1)\,Y_{km}(\Omega_2) \tag{A8}$$

and, comparing radial parts, we easily see that the double angular integration in Eq. (A7) is given by

$$\begin{aligned} &\int d\Omega_1 \int d\Omega_2\, \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\Pi(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ &\quad = 2\sum_{abk} f_k(a,b)\frac{2k+1}{4\pi} R_a^*(1)R_b^*(2)R_a(1)R_b(2)\frac{\delta(r_1-r_2)}{r_1^2} \\ &\quad + 2\sum_{abk} g_k(a,b)\frac{2k+1}{4\pi} R_a^*(1)R_b^*(2)R_b(1)R_a(2)\frac{\delta(r_1-r_2)}{r_1^2}. \end{aligned} \tag{A9}$$

This is the delta-function analog of Eq. (A6). Finally, completing the r_2 integration of Eq. (A7) and dividing by 4π, we obtain

$$P_2(r_1) = \sum_{abk} f_k(a,b)\,\mathfrak{F}^k(a,b;r_1) + \sum_{abk} g_k(a,b)\,\mathfrak{G}^k(a,b;r_1) \tag{A10}$$

where

$$\mathfrak{F}^k(a,b;r_1) = \mathfrak{G}^k(a,b;r_1) = \frac{2k+1}{8\pi^2} R_a^2(r_1)\,R_b^2(r_1). \tag{A11}$$

Thus, we have derived Eqs. (13) and (14) of the text.

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