Relationship between the Coulomb Integral U and the Stoner Parameter I

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Orbital Hartree-Fock and the local spin density approximations to exchange are compared. The self-exchange integrals calculated from the Hartree-Fock approximation are far larger than those calculated from the local spin density approximation. We suggest that, in metals where the exchange integrals are well shielded, a suitable functional for exchange may be obtained by scaling the orbital Hartree-Fock approximation to the local spin density approximation while retaining the stronger orbital dependence. Application to Fe and US produces good agreement with measurements.

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Spin density functional theory, in particular the local spin density approximation (LSDA), plays a fundamental role in the modern theory of *itinerant* magnetism in metals [1]. In this theory moment formation is driven by the spin polarization energy, $E_{\rm SP}^{\rm LSDA}$. In a much used, and often quite good approximation [2], $E_{\rm SP}^{\rm LSDA} = -\frac{1}{4}\sum_{ll'} J_{ll'}^{\rm LSDA} m_l m_{l'}$, where m_l is the lth partial magnetic moment and $J_{ll'}^{\rm LSDA}$ are the LSDA exchange interactions between shells l and l'. Since the spin up and spin down energy bands are split more or less uniformly in LSDA, as in the older but more empirical Stoner theory—I_S—a linear combination of the matrix elements $J_{ll'}^{\rm LSDA}$, is conventionally referred to as the Stoner parameter [3].

At least equally important is the theory of moment formation in highly correlated electron metals or impurities in metals. The formation of *local* moments is most often described in terms of Hubbard [4] or Anderson [5] models in which the numerical sophistication of self-consistent energy band calculations in LSDA is replaced by a more advanced model containing parameters that are somewhat difficult to calculate [6]. Nevertheless in the Hartree-Fock approximation (HFA) to the Anderson model, for example, the difference in energy between magnetic and nonmagnetic states contains a spin polarization energy which may be written $E_{\rm SP}^{A} = -\frac{1}{4}Um_{l=0}^2$ for an s band where here U is the full Coulomb integral and typically an order of magnitude greater than I_S. The large difference in the magnitudes of U and I has led to less consternation than it should because it is widely believed [7] that $E_{\rm SP}^{A}$ is the self-exchange energy gained in moment formation whereas I_S contains only interelectron—sometimes referred to as Hund's first rule—exchange. The reality is more subtle since $E_{\rm SP}^{\rm LSDA}$ contains both self-electronic and interelectronic exchange energies [8].

An enlightening way to compare LSDA with HFA is to consider, schematically, the hydrogen atom. In the supposed paramagnetic atom half of an electron is placed in each of the ± spin states. In terms of orbital HFA there are exchange interactions between each half of an electron in the paramagnetic case leading to an exchange energy of $-\frac{F^0}{4}$, in terms of the Slater integral, F^0, which in this case is U. In the spin polarized case the exchange energy of one electron with itself is $-\frac{F^0}{2}$ and the spin polarization energy is $-\frac{F^0}{4}$. Therefore the total exchange energy in the polarized case, $-\frac{F^0}{2}$, provides the exact self-interaction correction to the classical Coulomb energy and *the spin polarization energy equals the exchange energy in the paramagnetic state* (both $-\frac{F^0}{4}$)—a feature of orbital HFA which arises from the fact that the exchange energy is quadratic in the total numbers of parallel spins. In practice, we calculate the Coulomb energy in a self-consistent LSDA calculation to be 0.55 Ry, which corresponds to $U = 1.1$ Ry and the calculated Slater exchange integral is F^0=1.14 Ry [9].

In order to compare LSDA with HFA we have made calculations for a hydrogen atom with LSDA to exchange but with *correlation omitted.* In the paramagnetic state the total energy is calculated to be −0.813 Ry of which −0.376 Ry is exchange energy. Spin polarized hygrogen has a total energy of −0.914 Ry of which the exchange energy is −0.506 Ry and the self-interaction is not quite complete. More interesting, however, is that our calculated *total* exchange energies in HFA and LSDA are approximately equal but the relative exchange energies in the paramagnetic and spin polarized cases are quite different. Even without explicit inclusion of correlation energy the spin polarization energy in LSDA of 0.101 Ry is far smaller than the 0.275 Ry in HFA and the exchange energy in the paramagnetic state is correspondingly larger. The reason is that the spherical exchange hole which travels with the electron has a radius proportional to the cube root of the inverse density [10] and this leads to an exchange energy proportional to the density to the power of 4/3 which is much weaker than the quadratic dependence of HFA. Therefore the tendency to moment formation is suppressed in LSDA compared with HFA *even before the correlation energy is explicitly introduced.* In the derivation of the exchange functional in

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LSDA the self-interaction is not explicitly omitted since the exchange energy is just the HFA exchange energy of a homogeneous electron gas, $E_{\text{ex}} = -e^2Vk_F^4/4\pi^3$. However, that LSDA implicitly includes shielding corrections seems to us most likely. Clearly, in the case of hydrogen, the spin polarization energy is entirely self-exchange energy and should complete the self-interaction correction (SIC) [11].

When *correlation energy* is added to the functional [12] the total energy of the paramagnetic state of hydrogen calculated to be -0.924 Ry of which -0.500 Ry is exchange energy. The total energy of the spin polarized state is -0.993 Ry of which the exchange energy is -0.591 Ry [13]. The self-interaction correction is very nearly complete [11] and the spin polarization energy has been further reduced to 0.069 Ry. This comparison of LSDA with orbital HFA shows that in the spin polarization energy $U = I$ in principle, but that the calculated integrals are $F^0 = 1.14$ Ry and $I = 0.22$ Ry from the LSDA integral or 0.28 Ry from the spin polarization energy. Here lies the root of the problem. The integral entering an orbital theory and the same integral evaluated by approximating locally by a homogeneous electron gas at the same density are not remotely similar.

The original theory of moment formation in itinerant electron metals, by Slater [14], used orbital HFA to derive an expression for the spin polarization energy of an open shell, E_{SP}^S, of the same form as—but predating—$E_{\text{SP}}^{\text{LSDA}}$ with I_S replaced by the Slater exchange parameter, f, a linear combination of atomic Slater integrals, F^k, with the largest Coulomb integral, F^0 excluded. To explain how this came about we write the usual expression for the average exchange energy of unfilled valence shells in the usual way,

$$E^{\text{ex}} = -\frac{1}{2} \sum_{lm,l'm'} \langle lm, l'm'|g|l'm', lm\rangle n_{lm} n_{l'm'} \delta_{s_{lm},s_{l'm'}} , \tag{1}$$

where g is the Coulomb interaction, lm labels the orbitals and in an extended system, n_{lm}—which are *local* occupation numbers—are in general *nonintegral.* This expression is evaluated in terms of Slater integrals through a multipole expansion of the Coulomb interaction. The term $lm = l'm'$ is included in the sum but for *integral* occupation numbers the first term in the expansion, containing F^0, exactly cancels the spherical part of the *direct* Coulomb interaction [14,15]. Slater therefore removed this contribution but evaluated higher multipole contributions to the exchange interaction using nonintegral orbital occupation numbers, an inconsistency which has been remarked upon by several authors [5,16,17]. The correct expression for the spin polarization energy, including intershell exchange, is easily derived under the assumption that the spin orbitals are equally populated [14] with occupation numbers $n_{lm}^{\pm} = q_l^{\pm}/(2l+1)$, where $q_l^{\pm}$ is the number of electrons with l character and spin ±,

$$E_{\text{SP}}^S = -\frac{1}{4} \sum_{l,l'} V_{ll'} m_l m_{l'} . \tag{2}$$

The exchange integrals $V_{ll'}$ are given in terms of radial Slater exchange integrals $G_{ll'}^k$ by

$$V_{ll'} = \sum_k \begin{pmatrix} ll'k \\ 000 \end{pmatrix}^2 G_{ll'}^k , \tag{3}$$

where the term $k = 0$ is now included, $(\cdots)$ is a Wigner $3j$ symbol, and $G_{ll'} = F_{ll'}$ when $l = l'$. When $l = l' = 0$ Eqs. (2) and (3) reduce to $E_{\text{SP}}^S = -\frac{1}{4}F^0m^2$ and $F^0 = J_{\text{HFA}} = U$. More generally, but with $F^0 \gg F^k$ for $k > 0$ the $3j$ symbol $\left(\begin{smallmatrix} ll0 \\ 000 \end{smallmatrix}\right) = 1/\sqrt{2l+1}$ and $J_{\text{HFA}} = U/(2l+1)$. This relation is implicit in the work of Brandow [18] on Mott insulating transition metal compounds where the denominator is 5 for d states, but we are not aware that the more general form has been derived.

Despite the success of LSDA for metals the need for improvements in applications to narrow band metals has become evident. Recent extensions include orbital polarization [19] and self-interaction correction [11]. These extensions have in common that the energies of the individual orbitals depend upon their occupation rather than the total spin density as in LSDA. However, the exchange interactions in these orbital theories are expressed in terms of Slater exchange integrals which, if all are correctly included, yield exchange splittings that are too large in itinerant electron metals. It is notable, however, that if a shielded value for U is used instead of the bare Coulomb integral, the relation $J_{\text{HFA}} = U/(2l+1)$ yields an exchange interaction close to the the LSDA exchange integral. For example, we calculate for the $5f$ states of a uranium atom that $F^0 = U \approx 1$ Ry but that if the shielding of the $5f$ states by $6d$ states is included [17,20] U is reduced to between 2 and 3 eV and $U/7$ is about 0.3–0.4 eV compared with the LSDA exchange integral of 0.4 eV. Alternatively, shielded values of U may be deduced from experiments on metals [21] and again, upon dividing by $2l+1$, approximate agreement with the LSDA exchange integrals is obtained.

The formal exquivalence of U and I discussed above suggests a way to arrive at a theory of exchange orbital polarization which reduces to LSDA in the limit when each valence shell has equally populated orbitals. When the restriction to equal occupation used to arrive at Eq. (3) is removed the spin polarization energy becomes

$$E_{\text{SP}}^S = -\frac{1}{4} \sum_{l,l'} V_{ll'} m_l m_{l'} - \frac{1}{4} \sum_{lm,l'm'} V_{lml'm'} \delta m_{lm} \delta m_{l'm'} , \tag{4}$$

where

$$V_{lml'm'} = \sum_k [C(lm;l'm')]^2 G_{ll'}^k . \tag{5}$$

$C(lm;l'm')$ is a Gaunt coefficient and $\delta m_{lm} = m_{lm} - m_l/(2l+1)$ is the difference between the actual occupation and the average for a shell. Now if, when the orbital populations are equal, the exchange integrals from orbital HFA, $V_{ll'}$, are formally equivalent to the LSDA exchange integrals, $J_{ll'}$, Eq. (5) may be scaled using Eq. (3), whence

$$E_{\mathrm{SP}} = -\frac{1}{4}\sum_{l,l'} J_{ll'} m_l m_{l'} - \frac{1}{4}\sum_{lm,l'm'} \tilde{V}_{lml'm'} \delta m_{lm} \delta m_{l'm'} \ , \tag{6}$$

where

$$\tilde{V}_{lml'm'} = d_{lml'm'} J_{ll'}^{\mathrm{LSDA}} \tag{7}$$

and

$$d_{lml'm'} = \frac{\sum_k [C(lm;l'm')]^2 G_{ll'}^k}{\sum_k \begin{pmatrix} l l' k \\ 000 \end{pmatrix}^2 G_{ll'}^k} \ . \tag{8}$$

The spin polarization energy obtained from Eq. (6) depends upon the occupation of the individual orbitals, and the energies of the orbitals are shifted by amounts given by

$$\delta\epsilon_{lm}^{\pm} = \mp\frac{1}{2}\sum_{l'} J_{ll'}^{\mathrm{LSDA}} \left(m_{l'} + \sum_{m'} d_{lml'm'} \delta m_{l'm'} \right) \ . \tag{9}$$

Equations (6) and (8) are similar in form to the Wigner-Eckart theorem with the angular dependence contained in $d_{lml'm'}$, and the dynamics (including any effective screening) being in the "reduced matrix element" $J_{ll'}$. Clearly Eq. (6) reduces to LSDA when $\delta m_{lm'} = 0$.

The approximation to an energy functional introduced here is intended to be suitable for metals and metallic compounds when LSDA is itself a reasonable approximation but requires correction for orbital effects not present in the homogeneous electron gas. It is not intended for Mott-Hubbard insulators where U may well be less well shielded [17,18,22]. We have applied the present approximation in self-consistent calculations for Fe and US and calculated their spin and orbital moments. The results are shown in Table I. The former metal is important because its magnetic anisotropy and orbital moment have been the subject of several recent detailed studies [19,23]. In this case spin and orbital moments of $2.22\mu_B$ and $0.04\mu_B$, respectively, are obtained in LSDA. The moments are $2.22\mu_B$ and $0.06\mu_B$ in an orbital polarization scheme designed to incorporate the Hund's second rule in the electron gas [19]. In the present approximation the calculated orbital moment is increased (Table I), is greater than measured, but acceptable.

TABLE I. The calculated spin and orbital magnetic moments, in μ_B, of US ($5f$ contribution) and Fe using the present scheme. The experimental data are from Ref. [26].

		Fe	US
μ_S	Theory	2.13	1.51
μ_L	Theory	0.13	−3.12
μ_S	Exp.	2.13	1.31
μ_L	Exp.	0.09	−3.0

The compound US is a notoriously difficult case, evidently having itinerant $5f$ electrons but possessing an orbital moment larger than the spin moment [24]. In narrow band actinide compounds LSDA is severely tested and previous studies [19] have shown that although large orbital moments are induced by spin-orbit interaction ($\mu_S = 2.10\mu_B$ and $\mu_L = -3.2\mu_B$ for the $5f$ states in US) they are not large enough. With orbital polarization [19] the calculated moments were $\mu_S = 2.2\mu_B$ and $\mu_L = -4.0\mu_B$—leading to a considerable improvement in the calculated total moment. However, analysis of the magnetic form factor suggests that both the calculated spin and orbital moments were too large. The present approximation produces a considerable improvement (Table I), bringing both total magnetic moment and individual contributions to the magnetic moment into agreement with experiment. In particular, the reduction in the spin component of the moment with retention of a large orbital component is a feature demanded by analysis of recent experiments on uranium compounds [25].

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964); W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).

[2] O. Gunnarsson, J. Phys. F **6**, 587 (1976); J.F. Janak, Phys. Rev. B **16**, 255 (1977); M.S.S. Brooks and B. Johansson, J. Phys. F **13**, L197 (1983).

[3] E.C. Stoner, Proc. R. Soc. London A **154**, 656 (1936); **169**, 339 (1939).

[4] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963).

[5] P.W. Anderson, Phys. Rev. **124**, 41 (1961).

[6] O. Gunnarsson, Phys. Rev. B **41**, 514 (1990).

[7] See, e.g., V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B **44**, 943 (1991); R.E. Watson, J. Appl. Phys. **67**, 5535 (1990).

[8] B. Brandow, Adv. Phys. **26**, 651 (1977).

[9] The HFA integrals are very approximate since we have used self-consistent LSDA wave functions to calculate them. The argument is not affected, however, and the numerical approximations may be improved upon as desired.

[10] The argument leading to this result is well known and predates LSDA; see, e.g., J.C. Slater, *Quantum Theory of Matter* (McGraw-Hill, New York, 1968).

[11] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990); Europhys. Lett. **7**, 171 (1988); I.V. Solovyov, A.I. Liechtenstein, V.A. Gubanov, O. Gunnarsson, and R.O. Jones, Solid State Commun. **37**, 249 (1981); R.A. Heaton, J.G. Harrison, and C.C. Lin, Phys. Rev. B **28**, 5992 (1983).

[12] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972); L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[13] O. Gunnarsson, B.I. Lundqvist, and J.W. Wilkins, Phys. Rev. B **10**, 1319 (1974).

[14] J.C. Slater, Phys. Rev. **49**, 537 (1936); **165**, 655 (1968); **165**, 658 (1968); J.C. Slater, J.B. Mann, T.M. Wilson,

and J.H. Wood, Phys. Rev. **184**, 672 (1969).

[15] See also B. Coqblin and A. Blandin, Adv. Phys. **17**, 281 (1968).

[16] P. Wohlfarth, Rev. Mod. Phys. **25**, 211 (1953).

[17] C. Herring, *Exchange Interactions among Itinerant Electrons*, Magnetism, A Treatise on Modern Theory and Materials Vol. 4, edited by G.T. Rado and H. Suhl (Academic Press, New York, 1966).

[18] B. Brandow, J. Alloys Compounds **181**, 377 (1992), and references cited therein.

[19] M.S.S. Brooks, Physica (Amsterdam) **130B**, 6 (1985); O. Eriksson, M.S.S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990); O. Eriksson, B. Johansson, R.C. Albers, A.M. Boring, and M.S.S Brooks, Phys. Rev. B **42**, 2707 (1990).

[20] P.A. Cox and P. LLoyd, J. Phys. F **6**, 797 (1976); M.S.S. Brooks, B. Johansson, O. Eriksson, and H.L. Skriver, Physica (Amsterdam) **144B**, 1 (1986).

[21] See, e.g., D. van der Marel and G.A. Sawatzky, Phys. Rev. **37**, 10 674 (1988).

[22] M.R. Norman, Phys. Rev. Lett. **64**, 1163 (1990).

[23] See, e.g., G.H.O. Daalderop, P.J. Kelly, and M.F.H. Schuurmans, Phys. Rev. B **41**, 11 919 (1990); H.J.F. Jansen, J. Appl. Phys. **67**, 4555 (1990); R. Coehoorn and G.H.O. Daalderop, J. Magn. Magn. Mater. **104–107**, 1081 (1992); H. Ebert, P. Strange, and B.L. Gyoffry, J. Phys. F **18**, L135 (1988).

[24] J.M. Fournier and R. Troc, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A.J. Freeman and G.H. Lander (North-Holland, Amsterdam, 1984), Vol. 2, p. 29; G.H. Lander, M.S.S. Brooks, B. Lebech, P.J. Brown, O. Vogt, and K. Mattenberger, Appl. Phys. Lett. **57**, 989 (1990).

[25] B. Lebech, M. Wulff, G.H. Lander, J. Rebizant, J. Spirlet, and J. Delapalme, J. Phys. Condens. Matter **1**, 10 229 (1989).

[26] Experimental data for US are taken from the form factor of F.A. Wedgwood, J. Phys. C **5**, 2427 (1972), while for Fe we quote M. B. Stearns, in *Magnetic Properties of 3d, 4d, and 5d Elements, Alloys, and Compounds*, edited by H.P.J. Wijn, Landolt-Börnstein, New Series, Vol. III/19a (Springer, Berlin, 1986).