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Uniform susceptibilities of metallic elements

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The exchange-correlation enhanced spin susceptibilities of 32 metallic elements from Li through In have been calculated using the spin-polarized exchange-correlation functional of von Barth and Hedin. Since these 32 elements include both the $3d$ and $4d$ transition series, the calculations clearly exhibit both the normal trends with atomic number and the anomalies responsible for ferromagnetism. The susceptibilities were obtained by evaluating the Vosko-Perdew approximate formal solution of the linear-response problem for each element, using fully self-consistent nonmagnetic ground-state energy bands and wave functions. In addition, the accuracy of the Vosko-Perdew approximation itself was tested for Cr by performing a separate nonperturbative spin-polarized calculation of the response (for the same exchange-correlation functional) to an external magnetic field for this metal (the two susceptibilities agree to within 10%).

I. INTRODUCTION

Quantitative calculation of the properties of solids requires an adequate treatment of the electron-electron interaction, but this interaction is so difficult to deal with that approximations for the effects of exchange and correlation must be introduced.[1-3] The accuracy of these approximations is still an unsettled question, and, while they are simpler than the full interaction, they are nevertheless often of such complexity that the easiest way to test them is to see how well they agree with experiment.

This paper is concerned with the efficacy of the local-density theory of exchange and correlation for predicting ferromagnetism. This is studied by calculating the response of a number of metallic elements to a spatially uniform external magnetic field. If the exchange-correlation approximation being tested is of value, its enhancement of the response should be large enough to produce a ferromagnetic instability only in those metals which are known to be ferromagnetic.

Naturally, this is a valid test of the exchange-correlation approximation only if the procedure used to calculate the response introduces negligibly small errors. The main difficulty is the feedback effect of exchange and correlation, the simplest expression of which is the Stoner enhancement[4]; the magnetization depends not only on the external field, but also on the space-dependent internal exchange-correlation field, which in turn depends on the magnetization. Using perturbation theory on the ground state, this response problem can be formulated as an integral equation, as was done by Kohn and Sham[3] and more recently by Vosko and Perdew[5] (VP), but the quantities entering this integral equation are functionals of the ground-state properties of the system. This functional dependence is so complicated that VP further introduce a Stonerlike approximate formal solution of the integral equation, giving the magnetization in terms of much simpler ground-state quantities (this is justified because, as VP show, there is a variational principle for the susceptibility).

Vosko *et al.*[6] have calculated the susceptibilities of the alkali metals, and Gunnarsson[7] those of six transition metals, in this way. Vosko *et al.* performed self-consistent calculations, while Gunnarsson used approximate wave functions. The results presented in this paper for these and many more metals are based on fully self-consistent ground-state calculations.[8] The tendency toward magnetism is one of the most delicate properties of solids, because of the small energy changes involved, and it is of obvious importance to have accurate ground-state quantities. While satisfactory approximations may exist for particular materials (indeed, the present results are in excellent agreement with those of Gunnarsson, and differ from those of Vosko *et al.* only because of the use of different exchange-correlation approximations), self-consistent calculations afford a viable means of finding ground-state quantities for a wide class of materials in a systematic way, and furthermore eliminate one possible source of uncertainty in the computational chain.

There still remains the question of the accuracy of the approximate solution of the integral equation. For a given approximation for exchange and correlation, self-consistent spin-polarized energy-band calculations provide a means for calculating the exact response of a material to a uniform magnetic field. This procedure obviates the introduction of a linear integral equation for the response, or of any approximations necessary for its solution. Poulsen *et al.*[9] have found the susceptibilities of six transition metals with this procedure, using the linear-muffin-tin-orbital (LMTO) method of band calculation. However, a comparison of their results to, e.g., those of Gunnarsson[7] in order to test the approximate solution of the integral equation would not be conclusive, because of the different approximations these authors introduced. The "exact" procedure is carried through here for paramagnetic Cr [using the muffin-tin Korringa-Kohn-Rostoker (KKR) method, and thus introducing the same approximations as were used in the ground-state calculations[8]], and a comparison to the results obtained using self-consistent ground-state quantities in the approximate formal solution of VP shows that the latter is accurate to about 10% for this material.

The approximate VP solution is evaluated in this paper for 32 metallic elements ranging from Li to In, using the local form of the exchange-correlation functional $E_{\text{xc}}[\rho;m]$ proposed by von Barth and Hedin[10] (but with slightly different values of the constants). Application to such a wide class of materials, including the first two transition series, permits the study of trends, and provides an understanding of why, of all the elements considered, only Fe, Co, and Ni are theoretically found to be ferromagnetic.

In Secs. II and III, the approximate solution of VP is discussed; the results of the present calculations for the elements are described in Sec. IV, and the exact solution for Cr and its implications are discussed in Sec. V.

II. INTEGRAL EQUATION FOR m

As discussed by VP,[5] the magnetization $m(\vec{r})$ (in units of Bohr magnetons) of a paramagnet to lowest order in the external field $H_e(\vec{r})$ is the solution of the integral equation

$$m(\vec{r}) = \int d\vec{r}\,'\,\chi(\vec{r},\vec{r}\,')\,[H_e(\vec{r}\,') - K(\vec{r}\,')\,m(\vec{r}\,')]\,, \qquad (1)$$

where $\chi(\vec{r},\vec{r}\,')$ is the unenhanced real-space susceptibility [or equivalently the functional derivative $\delta m(\vec{r})/\delta H(\vec{r}\,')$, evaluated at $H=0$]. The term $K(\vec{r}\,')\,m(\vec{r}\,')$ under the integral represents an exchange-correlation enhancement of the field, and Eq. (1) thus expresses the response of the magnetization to the total effective field.

The form of $\chi(\vec{r},\vec{r}\,')$ is important in considering approximate solutions of Eq. (1). To find it, one examines the change in the magnetization

$$\begin{aligned} m(\vec{r}) &= \rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r}) \\ &= \sum_i \Theta(E_F - E_{i\uparrow})\,|\psi_{i\uparrow}|^2 - \sum_i \Theta(E_F - E_{i\downarrow})\,|\psi_{i\downarrow}|^2\,, \end{aligned} \qquad (2)$$

due to a perturbing Hamiltonian containing a field $\delta H(\vec{r}\,')$. Using first-order perturbation theory to find the change in the E_i's and ψ_i's, we find

$$\begin{aligned} \chi(\vec{r},\vec{r}\,') = {}& \sum_i \delta(E_F - E_i)\,|\psi_i(\vec{r})|^2\,|\psi_i(\vec{r}\,')|^2 \\ &+ \sum_{i\neq j} \frac{\Theta(E_F - E_i) - \Theta(E_F - E_j)}{E_j - E_i} \\ &\times \psi_i^*(\vec{r})\,\psi_j(\vec{r})\,\psi_j^*(\vec{r}\,')\,\psi_i(\vec{r}\,') \end{aligned} \qquad (3)$$

in the unpolarized limit. (The index i includes a band index, a wave vector, and a spin index; the spins of states i and j must be the same in the second sum.) The first sum in Eq. (3) comes from the change in the E_i's and the second from the change in the ψ_i's. This equation is basically the Lindhard expression, but the space dependence is that of the true wave functions rather than (for example) plane waves.[11] The intraband term [first sum in Eq. (3)] can be regarded as the limit as $i\to j$ of the term excluded from the second sum, and becomes $N(E_F)$, the density of states at the Fermi energy E_F, in the usual long-wavelength analysis of the Lindhard susceptibility.[12]

The quantity $K(\vec{r})$ in Eq. (1) is a kernel giving the exchange-correlation enhancement of the field due to the magnetization, and is defined by

$$\{\delta^2 E_{\text{xc}}[\rho;m]/\delta m(\vec{r})\,\delta m(\vec{r}\,')\}_{m=0} = 2K(\vec{r})\,\delta(\vec{r}-\vec{r}\,')\,, \qquad (4)$$

where $E_{\text{xc}}[\rho;m]$ is the exchange-correlation functional.[5,10] In general, the functional derivative in Eq. (4) has a complicated dependence on both $\vec{r}$ and $\vec{r}\,'$. It is proportional to a δ function only in the local approximation for E_{xc}, to which attention is restricted exclusively in this paper.

For consistency, the Bloch functions ψ_i and energies E_i appearing in Eq. (3) should be the solutions of the ground-state system of equations[13]

$$[-\nabla^2 + V_H(\vec{r}) + \mu_{\text{xc}}(\vec{r})]\,\psi_i(\vec{r}) = E_i\psi_i(\vec{r})\,, \qquad (5)$$

$$\begin{aligned} V_H(\vec{r}) = {}& -2Z\sum_{\vec{R}} |\vec{r}-\vec{R}|^{-1} \\ &+ 2\int \rho(\vec{r}\,')\,|\vec{r}-\vec{r}\,'|^{-1}\,d\vec{r}\,'\,, \end{aligned} \qquad (6)$$

$$\rho(\vec{r}) = \sum_i \Theta(E_F - E_i)\,|\psi_i(\vec{r})|^2\,, \qquad (7)$$

which constitute a nonmagnetic self-consistent energy-band problem. V_H is the Hartree potential (in Ry units), Z is the nuclear charge, and the $\vec{R}$'s are the nuclear coordinates. The exchange-correlation potential used in Eq. (5) is

$$\mu_{\text{xc}}(\vec{r}) = \{\delta E_{\text{xc}}[\rho;m]/\delta\rho(\vec{r})\}_{m=0}\,, \qquad (8)$$

where the functional E_{xc} should be the same as the one appearing in Eq. (4). Having solved this ground-state problem, one can (in principle) use the resulting eigenfunctions and eigenvalues to evaluate the susceptibility $\chi(\vec{r},\vec{r}\,')$, and then try to solve Eq. (1). Given the complicated form of $\chi(\vec{r},\vec{r}')$, and the slow convergence of the interband sum,[14] it is unlikely that this procedure is tractable for any real material.

However, the presence of a magnetic instability is presumably sensitive to the detailed form of the wave functions and band structure, and it is of great interest to have some way to obtain solutions of Eq. (1) which retain all the complications of the band structure inherent in $\chi(\vec{r},\vec{r}')$. For example, a nonzero solution, when H_e is an infinitesimal field varying as $\exp(i\vec{q}\cdot\vec{r})$, would correspond to a spin-density-wave instability of wave vector $\vec{q}$.[15] The standard approach[16] to this problem consists of searching for peaks in the Fourier transform of $\chi(\vec{r},\vec{r}')$ (usually replacing the Bloch functions by plane waves). This approach ignores the effects of the Bloch functions and the $\vec{r}$ dependence of $K(\vec{r})$ on possible instabilities, about which very little is known.

A numerical method exists for constructing the exact magnetization $m(r)$ induced by a uniform external field: for a given approximation for exchange and correlation, self-consistent spin-polarized energy-band computer programs (i.e., those appropriate for itinerant ferromagnets) can be used to find the response of a paramagnet to a uniform field of any strength, if the appropriate field term is added to the Hamiltonian. This is a nonperturbative calculation, in the sense that the wave functions and eigenvalues are found by self-consistently solving Schrödinger's equation in the presence of the field, and the magnetization is evaluated directly from the resulting charge densities, as in Eq. (2). If such a calculation is carried out for a sufficiently small external field (or if the linear response is extracted from calculations for several field strengths), the resulting magnetization $m(\vec{r})$ will be identical to the exact solution of Eq. (1) for the same field, and this can be used to check approximate solutions of this equation. A similar solution for fields with space dependence commensurate with the lattice requires a much more difficult supercell calculation (unit cell determined by the periodicity of the field, rather than that of the lattice), and the response to incommensurate fields cannot be found in this way at all. Thus it is presently relatively straightforward to find the response to external fields only in the uniform case.

III. APPROXIMATE SOLUTION

Given the complexity of $\chi(\vec{r},\vec{r}')$, it would be useful to have an approximate solution of Eq. (1). For a uniform field, an approximate formal solution, expressed in terms of the spin density $\gamma(\vec{r})$ induced by an infinitesimal Stoner splitting[17] of the actual bands, was suggested by VP,[5] and also concurrently by Gunnarsson.[7] Define

$$\gamma(\vec{r}) = \sum_i \frac{\delta(E_F - E_i)\,|\psi_i(\vec{r})|^2}{N(E_F)}\,, \tag{9}$$

where

$$N(E_F) = \sum_i \delta(E_F - E_i) \tag{10}$$

is the density of states at the Fermi energy. Because of the orthogonality of the Bloch functions, one has

$$\int \chi(\vec{r},\vec{r}')\,d\vec{r}' = \int \chi(\vec{r}',\vec{r})\,d\vec{r}' = N(E_F)\,\gamma(\vec{r}) \tag{11}$$

[the interband term in Eq. (3) does not contribute to these integrals]. Thus, for a uniform field, Eq. (1) becomes

$$m(\vec{r}) = H_e N(E_F)\gamma(\vec{r}) - \int d\vec{r}'\,\chi(\vec{r},\vec{r}')K(\vec{r}')m(\vec{r}')\,. \tag{12}$$

Now try an approximation of the form $m(\vec{r}) = C\gamma(\vec{r})$. Integrating Eq. (12) over $\vec{r}$ to determine C, and noting that

$$\int d\vec{r}\,\gamma(\vec{r}) = 1\,, \tag{13}$$

one finds

$$m(\vec{r}) = H_e N(E_F)\gamma(\vec{r}) \Big/ \left(1 + N(E_F)\int d\vec{r}'\,\gamma^2(\vec{r}')K(\vec{r}')\right). \tag{14}$$

Thus the uniform susceptibility is

$$\chi = N(E_F) \Big/ \left(1 + N(E_F)\int d\vec{r}\,\gamma^2(\vec{r})K(\vec{r})\right). \tag{15}$$

It happens that $K(\vec{r})$ is always negative,[5] so the connection to the usual expression for the exchange-enhanced susceptibility[4]

$$\chi = N(E_F)/[1 - N(E_F)I] \tag{16}$$

is made by defining the "exchange" integral as

$$I = \int d\vec{r}\,\gamma^2(\vec{r})\,|K(\vec{r})|\,. \tag{17}$$

However, this integral also includes correlation effects, because of the definition of $K(\vec{r})$ in Eq. (4).

VP have shown that there is a variational principle for χ^{-1}. This justifies the ansatz used to construct Eq. (14), and also shows that the quantities in Eqs. (15) and (16) are lower bounds to the correct results. VP give no estimates of the tightness of the bounds [although they point out that the variational principle implies that errors in χ should be second order in the error in $m(\vec{r})$], and one contribution of the present paper is to establish the accuracy of Eq. (15) by comparing to the exact initial ($H = 0$) susceptibility for Cr (calculated using the same approximation for E_{xc}).

Vosko *et al.*[6] and Gunnarsson[7] have found the susceptibility enhancement obtained from Eq. (15) or the exchange integral I from Eq. (17) for a few elements. Vosko *et al.*[6] performed calculations for the alkali metals, using a spherical-cell method to obtain the Fermi-surface wave functions and thus $\gamma(\vec{r})$. Gunnarsson[7] has carried out calculations of the integral I for several transition metals, using superposed atomic charge densities and renormalized-atom charge densities to form a crystal potential, and solving the Schrödinger equation at the Fermi energy to get an estimate of $\gamma(\vec{r})$. Poulsen *et al.*[9] used the LMTO method of band calculation, but carried out the solution in the presence of an external field, to find the integral I in the metals at the ends of the three transition series. In obtaining the results described below, the Bloch functions appearing in $\gamma(\vec{r})$, and the charge density needed to determine $K(\vec{r})$, have been determined from self-consistent band calculations.[8] Thus the prescription [Eqs. (4)–(9)] for evaluating the susceptibility from Eq. (15), given only an explicit form for the exchange-correlation functional E_{xc}, has been carried through with the introduction of only one approximation (the muffin-tin approximation).

IV. RESULTS

The densities of states at the Fermi energy $N(E_F)$ and the exchange-correlation integral I obtained from the nonmagnetic ground-state calculations[8,18–21] via Eq. (17) are given in Table I and plotted versus atomic number in Fig. 1. Also

TABLE I. Calculated spin susceptibilities of metals. a is the lattice constant in atomic units (bohr), $N(E_F)$ is the density of states (both spins) at the Fermi energy in states/Ry atom, I is the exchange-correlation integral defined in Eq. (17), $\gamma(0)$ is the value of the function defined in Eq. (9) at the nucleus, and χ/χ_0 is the susceptibility enhancement, $[1 - N(E_F)I]^{-1}$, negative values of which indicate a ferromagnetic instability. The molar susceptibility (emu/mole) is $2.376 \times 10^{-6}(\chi/\chi_0)N(E_F)$.

Element	Structure	a (a.u.)	$N(E_F)$ (Ry^{-1})	I (Ry)	$\gamma(0)$ (bohr^{-3})	χ/χ_0
Li	bcc	6.42	6.5	0.086	0.133	2.25
Be	fcc	5.96	0.73	0.078	0.350	1.06
Na	bcc	7.7	6.2	0.067	0.590	1.71
Mg	fcc	8.4	6.2	0.052	0.690	1.47
Al	fcc	7.6	5.6	0.045	1.09	1.34
K	bcc	9.45	9.9	0.049	0.877	1.95
Ca	fcc	10.0	21	0.037	0.160	4.49
Sc	bcc	6.74	33	0.025	0.0264	6.12
Sc	fcc	8.49	24	0.025	0.129	2.48
Ti	fcc	7.56	22	0.025	0.136	2.17
V	bcc	5.54	22	0.026	0.186	2.34
Cr	bcc	5.30	9.5	0.028	0.084	1.36
Mn	fcc	6.543	21	0.030	0.106	2.74
Fe	bcc	5.15	42	0.034	0.0459	−2.34
Co	fcc	6.448	27	0.036	0.0646	38.2
Ni	fcc	6.55	55	0.037	0.0809	−0.98
Cu	fcc	6.76	3.9	0.027	1.60	1.12
Zn	fcc	7.25	4.1	0.038	3.83	1.18
Ga	fcc	7.83	5.5	0.037	3.55	1.26
Rb	bcc	10.21	12	0.043	1.58	2.12
Sr	fcc	10.88	4.2	0.031	0.357	1.15
Y	fcc	9.23	19	0.024	0.234	1.88
Zr	bcc	6.54	17	0.023	0.392	1.67
Nb	bcc	6.2	19	0.022	0.668	1.72
Mo	bcc	5.89	8.9	0.022	0.318	1.23
Tc	fcc	7.28	17	0.022	0.341	1.57
Ru	fcc	7.2	15	0.022	0.296	1.52
Rh	fcc	7.24	18	0.024	0.247	1.79
Pd	fcc	7.42	31	0.025	0.252	4.46
Ag	fcc	7.79	3.7	0.030	3.31	1.12
Cd	fcc	8.40	4.9	0.032	5.50	1.18
In	fcc	8.95	6.8	0.030	5.44	1.26

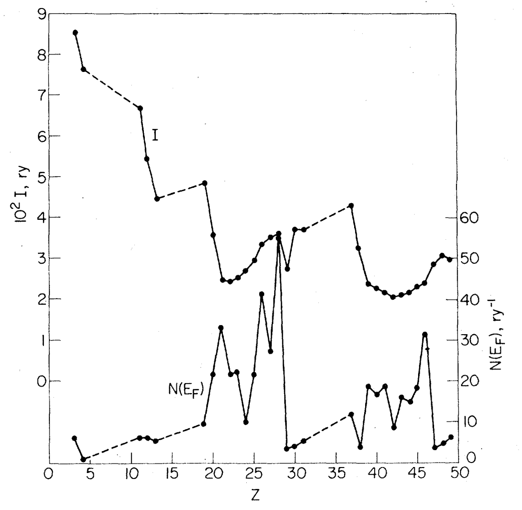

FIG. 1. Exchange-correlation integral I in Ry (upper curve; left scale) and density of states $N(E_F)$, both spins, in electrons/Ry atom (lower curve; right scale) as functions of atomic number Z. The zero of the left scale has been shifted, and dashed lines indicate ranges of Z for which calculations were not performed.

given in Table I is the quantity $\gamma(0)$, the function of Eq. (9) evaluated at the nucleus. This quantity, in conjunction with the other information in Table I, determines the magnetization $m(r=0)$ from Eq. (14), which in turn gives the conduction-electron contribution to the Knight shift.[22]

In all these calculations, the muffin-tin approximation was used.[23] The crystal structure was taken to be either bcc or fcc, and materials with hexagonal or more complicated structures were usually treated as fcc. For Sc, calculations were performed for both structures, and a comparison of the entries in Table I for this material shows that, while I is relatively insensitive to the crystal structure, the density of states is more sensitive. This can lead to large changes in the susceptibility enhancement with crystal structure.

For each material, the calculations were performed for the lattice constant given in Table I. This lattice constant is within 0.5% of the value for which the computed pressure is zero, but, for most of the materials in Table I, the predicted atomic volumes are a little smaller than experimental low-temperature values (the largest discrepancies in the atomic volume, about 10%, occur for the alkalis, but the agreement is much better for most of the other materials; see Ref. 8 for a detailed comparison).

Perhaps the most fundamental question about these results is the occurrence of ferromagnetism. Since, according to VP, Eq. (16) is a lower bound to the susceptibility, any material for which $N(E_F)I>1$ should be ferromagnetic. This definitely happens in Fe and Ni, and fcc Co is almost ferromagnetic $[N(E_F)I=0.97]$. Of the remaining elements considered, the largest susceptibility enhancements occur for (bcc) Sc $[N(E_F)I=0.84]$, Ca $[N(E_F)I=0.78]$, and Pd $[N(E_F)I=0.76]$; all the others are only moderately paramagnetic. A spin-polarized band calculation shows that fcc Co is in fact theoretically ferromagnetic at this lattice constant[24] (we earlier performed similar calculations[25] for Fe and Ni; see also Ref. 9). Equation (16) is a lower bound to χ, and this shows that it is in error by more than 3% for Co (a similar calculation for Cr, described below, implies a 10% error). The local-density theory (using the form of E_{xc} discussed in Ref. 18) thus (except for Co) correctly predicts the presence or absence of ferromagnetism in the elements through In.

There are three interesting aspects of the dependence of the exchange-correlation integral I on atomic number Z which are evident in Fig. 1: (a) the gradual overall decrease with increasing Z; (b) the more-or-less parabolic behavior within each transition series; and (c) the anomaly for Cu. The gradual decrease with atomic number is a consequence of the dependence of $K(\vec{r})$ on the total charge density $\rho(\vec{r})$: K varies roughly as $\rho^{-2/3}$ and, as $\rho(\vec{r})$ gradually increases with increasing Z, $|K(\vec{r})|$ and I gradually decrease.

The two remaining aspects of I vs Z are due to the same phenomenon. There are two characteristic forms for $\gamma(\vec{r})$: free-electron-like [$\gamma(\vec{r})$ roughly constant] and d-like [$\gamma(\vec{r})$ relatively peaked and localized within the unit cell]. Proceeding through a transition series, say from K through Ni, $\gamma(\vec{r})$ is initially free-electron-like for K, becomes a sum of free-electron and d contributions toward the middle of the transition series, and is primarily d-like toward the end of the series (Fe-Ni). We can model the effects of this behavior of $\gamma(\vec{r})$ on the integral I by considering the normalized linear combination $\cos^2\theta\,\gamma_1(\vec{r})+\sin^2\theta\,\gamma_2(\vec{r})$, where both γ_1 and γ_2 are normalized according to Eq. (13). If γ_1 is free-electron-like, and γ_2 is d-like, this linear combination mimics the change of $\gamma(\vec{r})$ through a transition series, if we let θ change gradually from zero to $\frac{1}{2}\pi$ as the atomic number is increased through the series. Because the coefficients of both $\gamma_1(\vec{r})$ and $\gamma_2(\vec{r})$ are less than unity, it is possible to use the Schwarz inequality to show[26] that the weighted integral of $\gamma^2(\vec{r})$ [i.e., the integral I of Eq. (17)] passes through a minimum as θ is increased from zero, and that the value of I at this minimum is less than either of the values of I which would have been obtained using $\gamma_1(\vec{r})$ or $\gamma_2(\vec{r})$ alone. Thus, in going through a transition series, I is largest at either end [fully free-electron-like or fully d-like $\gamma(\vec{r})$], and passes through a minimum near the middle of the series, when $\gamma(\vec{r})$ is a mixture of free-electron and d-like parts.

The anomaly for Cu is due to the same effect. Even though the d bands in Cu are filled, they are rather close to the Fermi level, and $\gamma(\vec{r})$ is still more than half d-like, due to s-d mixing; in consequence, its value of I is less than that for either Ni (fully d-like) or Zn (free-electron-like). This situation does not occur for Ag because its d bands are considerably lower than in Cu; the d contribution is relatively small, and $\gamma(\vec{r})$ is mostly free-electron-like.

It is apparent from Fig. 1 that ferromagnetism occurs basically because of the spatial localization of the d orbitals near the top of a d band. This localization produces *both* a large density of states (when the band is nearly full) and a relative maximum in the exchange-correlation integral I. The product $N(E_F)I$ is large enough for ferromagnetism at the end of the $3d$ series, but not the $4d$ series because the $4d$ wave functions must extend further out from the nucleus, which implies a larger interaction between neighbors, a larger bandwidth, and a smaller density of states. Even though the exchange-correlation integral is considerably larger in the light elements than in the $3d$ series, there is no possibility of ferromagnetism because of the much smaller densities of states. There is not much chance that metallic hydrogen will be ferromagnetic.

The values of I given in Table I for V, Fe, Co, Ni, and Pd are in excellent agreement[27] with those obtained by Gunnarsson,[7] and those for Fe, Ni, Rh, and Pd are in very good agreement with the results of Poulsen *et al.*[9]. Values of I for the alkali metals deduced from the results of Vosko *et al.*,[6] on the other hand, are about 20% lower than those given in Table I. This discrepancy is understandable in terms of differences in the approximations used for E_{xc}. These authors also used the von Barth-Hedin[10] functional form, but they used the random-phase approximation (RPA) values of the constants (as originally suggested by von Barth and Hedin[10]), whereas the results in Table I were obtained using the values of the constants given in Ref. 18.[28] Calculations were repeated for Li using the same E_{xc} as was used by Vosko *et al.*, leading to a value of I of 0.072 Ry, to be compared to the value of 0.086 Ry appearing in Table I, and the value of 0.070 Ry deduced from their results. It is remarkable that the exchange-correlation integral I is this sensitive to the detailed form of E_{xc}; this sensitivity offers real possibilities for accurately determining E_{xc} by comparison to experimental susceptibility enhancements. In this context, it should be pointed out that the results of Vosko *et al.*[6] are in better agreement with experimental [conduction-electron spin resonance (CESR) or spin-wave excitation] measurements of the spin susceptibilities of the alkali metals than are the present calculations. On the other hand, a recent measurement[29] in Al gives a *positive* Fermi-liquid B parameter, which, if interpreted directly in terms of a susceptibility enhancement, corresponds to a negative value of I. There is no reasonable local form for E_{xc} which gives a negative I, so that, unless for some reason the CESR or spin-wave experiments do not directly measure the static susceptibility enhancements discussed in this paper, this result indicates that there may be important nonlocal exchange-correlation effects on the susceptibility.

Because the calculated susceptibilities include only the spin paramagnetism, and thus the contributions from the cores and the orbital motion have been ignored, a detailed comparison with experimental bulk susceptibilities will not be made. It is of interest, however, that the calculated susceptibilities for the nonmagnetic members of both transition series are considerably smaller than the experimental values. This is understandable in terms of an orbital (Van Vleck) paramagnetism in non-s-band materials.[30] The size of the discrepancy between the present calculations and experiment is consistent, except for Pd, with both experimental[31-33] and theoretical[34,35] estimates of the orbital paramagnetism in various transition metals (as an example, $\chi_{\text{expt}}-\chi_{\text{spin}}$ for V is $+180 \times 10^{-6}$ emu/mole, while estimates[33-35] of its orbital paramagnetism range from 75 to 200×10^{-6} emu/mole). Also, the calculated spin susceptibility for Al agrees with the experimental bulk value, which might be taken as evidence for a small paramagnetic orbital term (just enough to cancel the Landau term) coming from p-like band states.

The calculated spin susceptibility enhancement for Pd is too small. The most likely explanation for this, aside from the fact that the calculations give a lower bound to χ, is that the density of states value in Table I is too small; an increase of only 15% in $N(E_F)$ is required to double the calculated susceptibility enhancement. The Fermi level in Pd, nonmagnetic Ni, and Ca (but none of the other elements in Table I) happens to fall at a point where the density of states is decreasing extremely rapidly with energy, making its value exceptionally sensitive to the Fermi-level position in these materials. It is thus quite possible for the density of states to be sizably changed by non-muffin-tin or relativistic effects (Mueller *et al.*[36] found a 10% increase in Pd due to the latter). Naturally, $N(E_F)$ for these materials will also be unusually sensitive to numerical tolerances in the calculation; for example, the estimated accuracy of the Fermi energy, $\pm 5\times 10^{-4}$ Ry, is enough to account for a 5% change in the density of states of Pd.

V. SOLUTION FOR Cr

Consider now an exact numerical calculation of the magnetization, to be carried out by performing self-consistent spin-polarized calculations in the presence of a magnetic field, as discussed above, and to be used to check the accuracy of the approximate solution given in Eq. (14). Note in particular that this approximate solution contains none of the interband part of the susceptibility [second sum in Eq. (3)] because of the orthogonality of the Bloch functions; $\gamma(\vec{r})$ depends only on the wave functions on the Fermi surface. Interband contributions can occur only when one of the two states (ψ_i, ψ_j) in the second sum in Eq. (3) is occupied and the other is empty. In a uniform field, one would expect the interband term to be important when the Fermi energy falls near the middle of a d-band complex, since there can then be a relatively large number of states satisfying these occupancy conditions, for which in addition the energy denominator is small. Therefore, it seemed that Cr would be an appropriate material on which to test Eq. (14).

Accordingly, a self-consistent spin-polarized calculation of the magnetization of Cr in a small uniform external field (field splitting of 2 mRy) was performed. The resulting susceptibility corresponded to an exchange integral [using Eq. (16)] of 0.031 Ry, compared to the approximate value of 0.028 Ry obtained from Eq. (17). This 10% agreement shows that the approximation to I given in Eq. (17) is remarkably accurate, and provides justification for asserting that the values of I in Table I for the other elements (and also those obtained by Vosko *et al.*[6] and Gunnarsson[7]) are probably within about 10% of the correct values for the assumed form for E_{xc}.[18] This conclusion is also supported by the results of Poulsen *et al.*[9]

The susceptibility enhancement of Cr is thus relatively small at $\vec{q}=0$. The situation at finite $\vec{q}$ is much more complicated. If we think in terms of a finite-$\vec{q}$ generalization of Eq. (16), of the form

$$\chi(\vec{q})=\chi^0(\vec{q})/[1-I_q\,\chi^0(\vec{q})]\,, \tag{18}$$

where $\chi^0(\vec{q})$ involves no matrix elements of Bloch functions, then, for a spin-density-wave instability to occur at finite $\vec{q}$,[15] either I_q or $\chi^0(\vec{q})$ must be much larger than at $\vec{q}=0$. A peak in $\chi^0(\vec{q})$ due to (imperfect) Fermi-surface nesting is the standard explanation of the antiferromagnetism of Cr (Ref. 16); it is often taken for granted in such investigations that I_q is large enough to produce the instability. However, of three calculations[37-39] of $\chi^0(\vec{q})$ for $\vec{q}$ at or near the nesting wavevector in Cr, only one, that of Asano and Yamashita,[39] gives a maximum value of $\chi^0(\vec{q})$ which is large enough to produce an instability if I_q is equal to the value of I in Table I. The rather large differences between the results of these calculations make it difficult to draw firm conclusions, but this is at least an indication that I_q at the nesting wave vector is larger than its value at $\vec{q}=0$, or possibly that Eq. (18) is a poor approximation to $\chi(\vec{q})$. Another, more serious implication is that a peak in $\chi^0(\vec{q})$ is not by itself sufficient evidence for an antiferromagnetic instability.

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[13] As pointed out by VP (Ref. 5), it is correct to use the ground-state eigenfunctions and eigenvalues to evaluate $\chi(\vec{r},\vec{r}\,')$, even though these eigenfunctions and eigenvalues have no direct physical meaning (the eigenvalues, for example, may not generate the correct Fermi surface). This is in distinction to the calculation of optical properties, where an excitation potential (see, e.g., Ref. 12) should be used instead of the ground-state potential.

[14] For high energy, the k^2 dependence of the energy denominator will be cancelled by the volume element in the k-space sum or integration. Thus the conver-

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[24] This calculation was not carried to full self-consistency, but only far enough to verify that ferromagnetism is present. The calculated moment of fcc Co at this lattice constant is about 0.2 μ_B. The presence of ferromagnetism is fairly structure sensitive (see entries in Table I for Sc; see also Ref. 9) and it may be that hcp Co will have a larger calculated moment at this atomic volume.

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[27] A factor of 2 must be allowed because of the different difinitions used for the density of states.

[28] The constants originally suggested by von Barth and Hedin (Ref. 10) were deduced from the RPA, and thus tend to overestimate correlation effects. This naturally leading to a smaller value of the exchange integral I. The constants used in this paper, as given in Ref. 18, are closer to present estimates of the optimum values [U. von Barth (private communication)].

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