

Ab Initio Calculation of the Spin Susceptibility for the Alkali Metals Using the Density-Functional Formalism*

S. H. Vosko, J. P. Perdew,[†] and A. H. MacDonald

Department of Physics and Erindale College, University of Toronto, Toronto, Canada

(Received 19 August 1974; revised manuscript received 2 June 1975)

The new variational-principle, density-functional theory of the spin susceptibility χ is used to make *a priori* calculations of χ for the alkalis. Crystalline effects are calculated by the spherical-cell method and the local spin-density approximation is used for the exchange-correlation functionals. The excellent agreement between the results and recent experiments establishes the validity of this new theory and the correctness of the theoretical values for the exchange-correlation enhancement of χ for a homogeneous electron gas for $r_s \lesssim 5$.

Recently the de Haas-van Alphen (dHvA) effect has been used to measure¹ the conduction-electron spin susceptibility χ for K, Rb, and Cs. These results have the potential, when combined with an appropriate theory, of extending our understanding of exchange and correlation (XC) effects of the lower-conduction-electron-density systems. χ is especially useful in this regard since it is essentially unaffected by the electron-phonon interaction while being very sensitive to exchange and correlation. Unfortunately the dHvA method only determines a series of possible values for χ and some theoretical guidance is necessary to choose the correct value (Cs in particular). Most theoretical work has concentrated on the XC enhancement for a homogeneous electron gas, χ_h/χ_0 , as a function of r_s and has resulted in a wide range of values, although a number of recent calculations² using different procedures agree to within a few percent. (χ_h and χ_0 are the susceptibilities of a homogeneous system with and without interactions, respectively, and r_s is the usual electron-density parameter.) The form of χ_h/χ_0 is only well established for $r_s \leq 1$ and although the above calculations are not based on simple expansions in r_s their validity for the range $r_s \approx 4$ to 6 remains in doubt.

When the above calculations are compared with experiment there are many large discrepancies.²

With regard to r_s in the range 5 to 6, Cs is especially important; however, after Li, Cs is the least free-electron-like of the alkalis. Therefore any theory for χ that is to further our understanding in this range of r_s must be capable of simultaneously treating band and XC effects. Such a theory³ has recently been developed and it is the purpose of this Letter to report calculations of χ for all the alkalis. The new formula for χ is based on a variational principle within the density-functional formalism of Hohenberg, Kohn, and Sham.⁴ It has the advantage of including the core-electron contribution to XC which is quite appreciable for the heavier alkalis. One of the ingredients of the theory is χ_h/χ_0 for a range of densities; thus it provides information on this quantity indirectly.

The new VP variational formula for χ is based on two theorems⁴ for electrons in external scalar and magnetic fields $v(\vec{r})$ and $B(\vec{r})$: (i) The ground-state energy is a functional of $n(\vec{r})$ and $\mathfrak{M}(\vec{r})$, the electron number and magnetic moment densities, i.e., $E_{v,B}[n, \mathfrak{M}]$. In particular the kinetic and the XC energies may be expressed by a universal functional $G[n, \mathfrak{M}]$. (ii) $E_{v,B}$ is stationary with respect to variations in $n(\vec{r})$ and $\mathfrak{M}(\vec{r})$ and the correct $n(\vec{r})$ and $\mathfrak{M}(\vec{r})$ make it a minimum. For a paramagnetic system (small \mathfrak{M}) it is sufficient to expand G about the $\mathfrak{M}=0$ value:

$$G[n, \mathfrak{M}] = G[n] + \frac{1}{2} \int d^3r d^3r' \mathfrak{M}(\vec{r}) G[\vec{r}, \vec{r}'; n] \mathfrak{M}(\vec{r}') + \dots, \quad (1)$$

where $G[\vec{r}, \vec{r}'; n]$ is a functional of n and plays the central role in the theory. From the stationary property of $E_{v,B}$ with respect to variations in n and \mathfrak{M} it follows⁴ that to first order in B , n is unchanged from the $\mathfrak{M}=0$ situation and

$$B(\vec{r}) = \int d^3r' G[\vec{r}, \vec{r}'; n] \mathfrak{M}(\vec{r}'). \quad (2)$$

KS determine the susceptibility functional $\chi[n]$ by introducing the paramagnetic response functional

$G^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ with which (2) can be inverted to yield

$$\mathfrak{M}(\tilde{\mathbf{r}}) = \int d^3r' G^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] B(\tilde{\mathbf{r}}'), \quad (3)$$

$$\chi[n] = \Omega^{-1} \int d^3r d^3r' G^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n], \quad (4)$$

where Ω is the crystal volume. As pointed out by KS Eq. (4) is completely general and exact. However, the functionals $G[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ and $G^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ are essentially unknown. KS obtain an approximate formula for $\chi[n]$ by noting that if the XC dependence of $G[n, \mathfrak{M}]$ on \mathfrak{M} is neglected (denote the corresponding functionals by $G_s[n, \mathfrak{M}]$, $G_s[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$, and $G_s^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$) $\chi[n]$ becomes $\chi_s[n]$, the usual band-theory result, and retaining the zeroth-order term in a ∇n expansion of $G^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] - G_s^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$:

$$\chi[n] \approx \chi_s[n] + \Omega^{-1} \int d^3r [\chi_h(n(\tilde{\mathbf{r}})) - \chi_0(n(\tilde{\mathbf{r}}))]. \quad (5)$$

Although the KS formula (5) does represent an advance over previous work⁵ it is inadequate for systems where crystalline effects are important because it makes the slowly varying approximation not only upon the XC energy but also upon a part of the kinetic energy.

The VP approach is based on variational principle, namely that $\chi^{-1}[n]$ is given by the minimum of

$$\chi^{-1}[n, \mathfrak{M}] = \Omega \int d^3r d^3r' \mathfrak{M}(\tilde{\mathbf{r}}) G[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] \mathfrak{M}(\tilde{\mathbf{r}}') / \left[\int d^3r \mathfrak{M}(\tilde{\mathbf{r}}) \right]^2 \quad (6)$$

with respect to variations in $\mathfrak{M}(\tilde{\mathbf{r}})$, and the fact that an exact expression for $G_s^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ can be obtained from the KS "single-particle-equations method." The latter makes it possible to express χ in terms of readily obtainable functionals, i.e., $G_s^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ and $G_{xc}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] \equiv G[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] - G_s[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$, by introducing the XC-enhanced internal field $b(\tilde{\mathbf{r}})$ through

$$\mathfrak{M}(\tilde{\mathbf{r}}) = \int d^3r' G_s^{-1}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] b(\tilde{\mathbf{r}}'). \quad (7)$$

Using as a trial function for $\mathfrak{M}(\tilde{\mathbf{r}})$ in (6) that generated by $b(\tilde{\mathbf{r}})$ a constant in (7) we obtain

$$\chi[n] \geq \frac{\chi_s[n]}{1 + \chi_s[n] \Omega \int d^3r d^3r' \gamma[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] G_{xc}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n] \gamma[\tilde{\mathbf{r}}', n]}, \quad (8)$$

$$\gamma[\tilde{\mathbf{r}}; n] \equiv \sum_i \delta(\mu - \epsilon_i) |\varphi_i(\tilde{\mathbf{r}})|^2 / \sum_i \delta(\mu - \epsilon_i), \quad (9)$$

where the $\varphi_i(\tilde{\mathbf{r}})$ are the self-consistent solutions of KS single-particle equations with eigenvalues ϵ_i , the chemical potential μ is determined so that the total number of electrons N equals $\sum_i \theta(\mu - \epsilon_i)$ which defines an auxiliary "Fermi surface" (FS) in distinction to the true FS,⁶ and $\chi_s[n] = \mu_e^{-2} g_s(\mu)$ with $g_s(\mu)$ the single-particle density of states at the auxiliary FS.

It should be emphasized that the use of a constant for $b(\tilde{\mathbf{r}})$ to produce a trial $\mathfrak{M}(\tilde{\mathbf{r}})$ does not mean that the XC enhancement of $b(\tilde{\mathbf{r}})$ is being neglected. The errors produced by the right-hand side of Eq. (8) are second order in the deviations of $b(\tilde{\mathbf{r}})$ from some optimum constant enhancement. Equation (8) is reminiscent of forms for χ derived for transition metals⁵ and its denominator represents the XC enhancement of χ over the usual band-theory result. The fact that γ and G_{xc} are functions of position is extremely important in accounting for the inhomogeneous nature of real systems including the effect of the core electrons since n is the total electron density.

The exact form for $G_{xc}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]$ is unknown. However, there is evidence that the local spin-density approximation for G_{xc} is adequate. It results in (VP)

$$G_{xc}[\tilde{\mathbf{r}}, \tilde{\mathbf{r}}'; n]_L = [\chi_h^{-1}(n(\tilde{\mathbf{r}})) - \chi_0^{-1}(n(\tilde{\mathbf{r}}))] \delta(\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'). \quad (10)$$

With substitution of (10) in Eq. (8) it follows that

$$\frac{\chi}{\chi_0(r_s)} \simeq \frac{m_s/m}{1 + (m_s/m) \chi_0(r_s) \Omega \int d^3r \gamma^2[\tilde{\mathbf{r}}; n] [\chi_h^{-1}(n(\tilde{\mathbf{r}})) - \chi_0^{-1}(n(\tilde{\mathbf{r}}))]}, \quad (11)$$

where we have introduced the single-particle auxiliary-FS density-of-states mass m_s so that $\chi_s = (m_s/m) \chi_0(r_s)$.

The self-consistent solution of the KS single-particle equations were found in a spherical-cellular approximation by use of the Kohn⁷ varia-

tional method. Following the usual prescription, the local density approximation⁸ was used for $E_{xc}[n]$. The number densities for core electrons were taken from atomic Hartree-Fock calculations⁹ and kept fixed in the determination of the

TABLE I. Comparison of various theories for $\chi/\chi_0(r_s)$ with experiment: Eq. (12)—lattice potential included by effective mass only with XC treated as in homogeneous case neglecting core effects; Eq. (13)—static dielectric screening by the ionic cores of conduction $e-e$ interactions and lattice potential included by effective mass only; Eq. (5)—KS formula; Eq. (11)—VP variational-principle results. CESR is conduction-electron spin resonance.

Ele.	r_s	m_s/m	r_s^*	$\frac{\chi_h(r_s)}{\chi_o(r_s)}$	Eq. (12)	Eq. (13) r_s^*	Eq. (5) KS	Eq. (11) VP	CESR ^{a,b,c} dHvA ^e	SPIN WAVE ^d
Li	3.26	1.47	4.71	1.47	2.79	2.57	1.95	2.66	2.50±.05 ^a 2.64±.13 ^b	-
Na	3.99	1.04	3.84	1.60	1.70	1.63	1.63	1.62	1.65±.05 ^a 1.72±.08 ^c	1.58±.09
K	4.86	1.07	4.39	1.78	2.03	1.79	1.82	1.79	1.701±.003 ^e	1.69±.07
Rb	5.20	1.05	4.33	1.87	2.07	1.75	1.87	1.78	1.724±.008 ^e	1.59±.12
Cs	5.62	1.18	4.83	2.01	2.89	2.10	2.08	2.20	1.76 ^e or 2.24 ^e ±.06 ±.06	-

^aKushida, Murphy, and Hanabusa, Ref. 10.

^bKettler, Shanholtzer, and Vehse, Ref. 11.

^cSchumacher and Vehse, Ref. 12.

^dDunifer, Pinkel, and Schultz, Ref. 13.

^eKnecht, Ref. 1.

self-consistent valence ϕ_i 's. In evaluating (11) and (5) we have used values of χ_h/χ_o given by von Barth and Hedin.² The results for m_s and χ from Eq. (11) for the alkalis are reported in Table I, along with the results of the KS formula (5) and, for the purpose of comparison, experimental values for χ as well as the predictions of other formulas which will be discussed below.

An often used formula¹⁴ for χ to include XC is

$$\chi^{-1} = \chi_b^{-1} + \chi_h^{-1}(r_s) - \chi_o^{-1}(r_s), \quad (12)$$

where $\chi_b = (m_b/m)\chi_o(r_s)$ and m_b/m is the band-structure enhancement of the density of states. This formula is derived by assuming that the XC for a metal is the same as for a homogeneous electron gas of the same conduction-electron density, while the Hartree field is included in the band structure. Equation (12) follows from (11) on taking the electrons at the auxiliary FS to be plane waves so that $\gamma[\vec{r}; n] \rightarrow 1/\Omega$ and taking $n(\vec{r})$ in χ_h^{-1} and χ_o^{-1} to be the average conduction-electron density. Thus, from our viewpoint, (12) may be regarded as a crude approximation to (11). In particular (12) fails to include the influence of the core electrons on the XC enhancement of χ . In fact, as seen in Table I, its agreement with experiment worsens progressively as we consider larger core systems. (In preparing Table I we have arbitrarily taken $m_b = m_s$.)

To account simultaneously for band effects and the influence of the core on XC, following a suggestion of Hedin,¹⁵ a model Hamiltonian can be introduced (VP). This leads to

$$\chi/\chi_o(r_s) = (m_b/m)[\chi_h(r_s^*)/\chi_o(r_s^*)], \quad (13)$$

where $r_s^* = (m_b/m)r_s/\epsilon$ and ϵ is the dielectric constant due to the cores.¹⁶ This gives considerable improvement over Eq. (12) (see Table I) and indicates the importance of the influence of the core electrons on XC. From Hedin's analysis this model is only applicable to systems which have small cores and whose conduction electrons are free-electron-like. In such cases the introduction of the dielectric constant due to the cores in the $e-e$ interaction while treating the electrons as free with a band mass accounts for the gross features of the core on XC. Thus Eq. (13) works reasonably well for the alkalis which satisfy these conditions, but is already insufficient to describe the volume dependence¹⁰ of $\chi/\chi_o(r_s)$ for Li.

As expected the KS formula (5) fails whenever m_s is large and is especially poor for Li. The VP formula (11) is in good agreement with experiment for the entire series of alkali metals. This is because it simultaneously includes crystalline effects, and the influence of the core electrons on XC. Theory unambiguously requires

$n(\vec{r})$ to be the total electron density; however, if we had incorrectly used only the valence electron density in Eqs. (10) and (11) the results would have been similar to those obtained from Eq. (12). Thus we see that by using the total electron density in G_{xc} the influence of the core electrons on XC is properly accounted for.

The validity of the VP theory is established by the success of its predictions for Li and Na where there is little doubt about the values of χ_h/χ_0 since $r_s \lesssim 4$, and where χ has been measured directly.¹⁰⁻¹² Furthermore, for K and Rb the VP predictions for χ differ from the dHvA values by at most 5% and the existence of spin-wave measurements removes the ambiguity in the dHvA method. If we consider the fact that the calculations have been done in the spherical-cell approximation this level of agreement suggests the correctness ($\pm 5\%$) of recent calculations of χ_h/χ_0 for $r_s \lesssim 5$. Unfortunately, for Cs there are only the dHvA results which admit two plausible values of χ/χ_0 (1.76 and 2.24). Our calculation indicates strongly that the higher value is correct, but this is dependent upon the spherical-cell approximation for calculating m_s (and $\gamma[\vec{r}; n]$) and upon the use of χ_h/χ_0 for $r_s \lesssim 5.6$ where the calculations are most uncertain. Therefore, measurements of χ that could distinguish between the two plausible dHvA values would be very helpful in furthering our understanding of XC effects in the range $4.5 \lesssim r_s \lesssim 5.6$.

We wish to thank Professor Shoenberg and Dr. Knecht for making their results available to us prior to publication.

*Work supported in part by the National Research Council of Canada and in part by the U. S. National Science Foundation.

†Present address: Rutgers University, New Brunswick, N. J. 08903.

¹B. Knecht, Ph.D. thesis, Cambridge University, 1974 (unpublished), and to be published.

²D. R. Hamann and A. W. Overhauser, Phys. Rev. **143**, 183 (1966); R. Dupree and D. J. W. Geldart, Solid State Commun. **9**, 145 (1971); U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. **5**, 1629 (1972); P. Vashishta and K. S. Singwi, Solid State Commun. **13**, 901 (1973).

³S. H. Vosko and J. P. Perdew, Can. J. Phys. **53**, 1385 (1975) (referred to as VP).

⁴P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965) (referred to as KS).

⁵C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. IV.

⁶M. Rasolt and S. H. Vosko, Phys. Rev. Lett. **32**, 297 (1974).

⁷W. Kohn, Phys. Rev. **96**, 590 (1954).

⁸B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

⁹E. Clementi, IBM J. Res. Dev. **9**, 2 (1965).

¹⁰T. Kushida, J. C. Murphy, and M. Hanabusa, Solid State Commun. **15**, 1217 (1974).

¹¹J. E. Kettler, W. L. Shanholzer, and W. E. Vehse, J. Phys. Chem. Solids **30**, 665 (1969).

¹²R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297 (1963).

¹³G. Dunifer, D. Pinkel, and S. Schultz, Phys. Rev. B **10**, 3159 (1974), and private communication.

¹⁴J. B. Sampson and F. Seitz, Phys. Rev. **58**, 663 (1940); S. Silverstein, Phys. Rev. **130**, 1703 (1963).

¹⁵L. Hedin, Ark. Fys. **30**, 231 (1965).

¹⁶J. R. Tessman, H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953); U. S. Whang, E. T. Arakawa, and T. A. Callcott, Phys. Rev. B **6**, 2109 (1972).

Si(111):SiH₃—A Simple New Surface Phase

K. C. Pandey, T. Sakurai, and H. D. Hagstrum

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 20 October 1975)

Photoemission spectra show that atomic hydrogen reacts near room temperature with Si(111)1×1 to form a trihydride phase, Si(111):SiH₃. The new phase, clearly to be distinguished from the monohydride Si(111):H obtained from Si(111)7×7, has been identified by theoretical calculation of the photoemission spectrum. Formation of Si(111):SiH₃ suggests that the vacancies that exist on clean Si(111)7×7 are disordered on Si(111)1×1.

In several recent studies chemisorption of oxygen^{1,2} and hydrogen^{3,4} on various semiconductor surfaces has been investigated by energy-loss, ion-neutralization, and ultraviolet-photoemission spectroscopies (UPS). For each of the surfaces studied it was concluded that the adsorbate atom

forms bonds with surface atoms of the equilibrium clean surface. For the particular case of atomic hydrogen adsorbed to the annealed Si(111)7×7 surface, theory^{5,6} and experiment⁴ agree in suggesting that the H atoms bond to the single dangling orbital per Si atom to form what we