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Theory of Core-Electron Contributions to Hyperfine Interactions*

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A convenient method is devised for the calculation of magnetic hyperfine constants in atoms, molecules, and metals taking into consideration the exchange interaction between the core electrons and the unpaired valence electrons. In this method, the core-electron wave functions are perturbed by the nuclear magnetic moment via the Fermi contact term, and the energy of the system is then calculated in the Hartree-Fock approximation using the perturbed core wave functions. The present method is closely related to the exchange perturbation method of Cohen, Goodings, and Heine. However, the former has the advantage of being more flexible in the sense that the same perturbed core-electron functions may be used for the ground and excited states of the atom and for metals without significant error. For lithium atom $1s^22s$ and $1s^22p$ states, we obtained values for the core contribution to the hyperfine constant a (in $a\mathbf{I}\cdot\mathbf{S}$) of 83.76 Mc/sec and -8.9 Mc/sec in good agreement with the earlier values of Cohen, Goodings, and Heine. We have applied this method to a calculation of the core-polarization correction to the Knight shift in lithium metal using recent wave functions of Kohn and Callaway. The core-polarization corrections produced by the s and p parts of the conduction-electron wave function are nearly equal but opposite in sign, while that produced by the d part is an order of magnitude smaller. This results in a net correction of about -5.3% of the direct contribution to the Knight shift from the conduction electrons.

I. INTRODUCTION

A NUMBER of recent detailed and careful investigations[1–10] of the magnetic hyperfine interaction in atoms and paramagnetic ions have clearly demonstrated the important role of exchange polarization of the core electrons in contributing to the magnetic hyperfine interaction constant. In all these investigations, the method that has been employed has come to be known generally as the unrestricted Hartree-Fock (UHF) method. In keeping with the recent attempt of standardization of nomenclature,[11] we shall call the unrestricted Hartree-Fock method the spin polarized method (SP). Similarly, the projected unrestricted Hartree-Fock method will be denoted as the projected spin polarized method (PSP).[12] Some of the investigators[2–4,6,9] have handled the SP method self-consistently, while others have used a perturbation approach. To avoid confusion we shall refer to the method of treating the exchange potential as a perturbation, the exchange perturbation method (EP). In recent papers, Nesbet,[7] Marshall,[8] and Heine[13] have discussed possible errors that can occur in the results of calculation by the SP method, because the many-electron wave function used in the SP method is not an eigenfunction of $\mathbf{S}^2$, where $\mathbf{S}$ is the total spin of the atom. From the investigations of these authors, one arrives at the conclusion, that for paramagnetic ions and atoms, this limitation of the SP method is not a serious source of error; but in extending the SP method to metals and molecules, one has to be more careful about the influence of this source of error.

In this paper we are interested in a perturbation method which has the advantage of flexibility over the EP method while not sacrificing accuracy. The accuracy

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* Supported by the National Science Foundation.

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[12] The PSP method should be distinguished from the SPP method. In the SPP method one applies the projection operator after an SP calculation is performed to obtain an eigenfunction of $\mathbf{S}^2$.

[13] V. Heine (to be published).

of the method can be easily compared with other perturbation calculations, which we shall show to be exactly equivalent in principle to our method. Specifically, what one does is to perturb the core electrons with the nuclear magnetic moment ($\boldsymbol{\mu}$) via the Fermi contact interaction; and with these perturbed functions, one then computes the energy to first order in $\boldsymbol{\mu}$, which is directly related to the hyperfine coupling constant. This method, which we shall call the moment perturbation method (MP), differs from the EP approach only in the order of application of the perturbations, since there the core electrons are perturbed by the exchange potential rather than the nuclear magnetic moment. The flexibility of the method arises by letting the nucleus perturb the core functions and approximating (which we demonstrate by our lithium atom calculations to be a good approximation) these perturbed functions as being independent of the configuration of the outer valence electrons. Thus, we assume that the interaction between the magnetic moment of the nucleus and the core electrons of the atom is not greatly altered when one goes from the atomic ground state to an excited state, or to molecular and metallic states. This has the advantage of enabling one to calculate exchange-polarization effects when the system is in a variety of environments without having to solve separate differential equations in each case. In order to demonstrate the practicality and flexibility of the MP method, we have calculated the hyperfine interaction constants for atomic lithium in the $1s^22s$ and $1s^22p$ configurations, and compared them with the results of earlier calculations. We then apply the MP method to calculate the contribution of exchange polarization to Knight shift in metallic lithium. In all these calculations, the perturbed core wave functions used were those calculated for atomic lithium $1s^22p$ configuration. This procedure[14] is analogous to similar cross perturbation methods that have been used for the quadrupole antishielding factors for ions,[15] and for the calculation of nuclear magnetic shielding coefficients in molecules.[16]

In Sec. II we describe the details of our method and its correspondence with the EP method. In Sec. III the method is applied to lithium atom $1s^22s$ and $1s^22p$ states, and the results are compared with earlier EP calculations. In Sec. IV we calculate the core-polarization correction to the Knight shift in lithium metal using the recent Wigner-Seitz wave functions obtained by Kohn and Callaway.[17] In Sec. V we shall discuss the limitations of the MP method and the problem of self-consistency.

THEORY OF THE MP METHOD

The general procedure followed here is similar to that employed in some other perturbation problems. However, for the sake of completeness, we have presented here an adaptation pertinent to our problem at hand. Let us consider a general system whose unperturbed Hamiltonian is $\mathcal{H}_0$ and whose ground-state wave function is Ψ_0.

$$\mathcal{H}_0\Psi_0=E_0\Psi_0. \tag{1}$$

Let the system be perturbed by two general first-order perturbing forces described by Hamiltonians $\mathcal{H}_E$ and $\mathcal{H}_N$. If $\delta\Psi_E$ and $\delta\Psi_N$ represent the first-order changes in the wave function of the system due to $\mathcal{H}_E$ and $\mathcal{H}_N$, respectively, then the energy of the system correct to the second order is

$$E=\frac{\langle\Psi_0+\delta\Psi_E+\delta\Psi_N|\mathcal{H}_0+\mathcal{H}_E+\mathcal{H}_N|\Psi_0+\delta\Psi_E+\delta\Psi_N\rangle}{\langle\Psi_0+\delta\Psi_E+\delta\Psi_N|\Psi_0+\delta\Psi_E+\delta\Psi_N\rangle}. \tag{2}$$

On simplication, after making a binomial expansion of the denomintaor, one gets

$$\begin{aligned}E=\{&E_0+E_e+E_N+2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_E\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_E\rangle\\&+2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_N\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_N\rangle+\langle\delta\Psi_E|\mathcal{H}|\delta\Psi_E\rangle\\&+\langle\delta\Psi_N|\mathcal{H}|\delta\Psi_N\rangle+2\langle\delta\Psi_E|\mathcal{H}_0|\delta\Psi_N\rangle\}\\&\quad-\{\langle\delta\Psi_E|\delta\Psi_E\rangle-\langle\delta\Psi_N|\delta\Psi_N\rangle-2\langle\delta\Psi_E|\delta\Psi_N\rangle\}.\end{aligned} \tag{3}$$

After omitting terms higher than second order, Eq. (3) becomes

$$\begin{aligned}E=E_0+E_e+E_N&+\langle\delta\Psi_N|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\\&+\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_E\rangle+2\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\\&+2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_E\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_E\rangle\\&\quad+2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_N\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_N\rangle,\end{aligned} \tag{4}$$

where we have assumed that the perturbed wave function is normalized to first order. That is,

$$\langle\Psi_0|\delta\Psi_E\rangle=\langle\Psi_0|\delta\Psi_N\rangle=0, \tag{5}$$

and the first-order changes in energy are given by

$$\begin{aligned}E_e&=\langle\Psi_0|\mathcal{H}_E|\Psi_0\rangle,\\E_N&=\langle\Psi_0|\mathcal{H}_N|\Psi_0\rangle.\end{aligned} \tag{6}$$

The second-order change in energy is given by

$$\begin{aligned}E^{(2)}=2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_E\rangle&+\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_E\rangle\\&+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_N\rangle+\langle\delta\Psi_N|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\\&+2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_N\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_E\rangle\\&\quad+2\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_N\rangle.\end{aligned} \tag{7}$$

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[14] While this work was in progress, we received a preprint of a paper by Heine (Ref. 13) in which he mentioned that E. Šimánek had independently proposed a similar method to Heine to avoid some of the inaccuracies of the SP method that were discussed in Ref. 13.

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The terms in the second-order change in energy can be regrouped[18] as

$$
\begin{aligned}
E_e^{(2)} &= 2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_E\rangle+\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_E\rangle\,,\\
E_N^{(2)} &= 2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_N\rangle+\langle\delta\Psi_N|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\,,\\
E_{eN}^{(2)} &= 2\langle\Psi_0|\mathcal{H}_E|\delta\Psi_N\rangle+2\langle\Psi_0|\mathcal{H}_N|\delta\Psi_E\rangle\\
&\quad +2\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\,.
\end{aligned}
\tag{8}
$$

The quantity $E_e^{(2)}$ is the second-order change in energy due to $\mathcal{H}_E$ alone; $E_N^{(2)}$ is the second-order change in energy due to $\mathcal{H}_N$ alone; and $E_{eN}^{(2)}$ is the second-order change in energy due to the interaction of $\mathcal{H}_E$ and $\mathcal{H}_N$.

The first-order equations for $\delta\Psi_E$ and $\delta\Psi_N$ are

$$(\mathcal{H}_0-E_0)\delta\Psi_E=-(\mathcal{H}_E-E_e)\Psi_0\,, \tag{9}$$

$$(\mathcal{H}_0-E_0)\delta\Psi_N=-(\mathcal{H}_N-E_N)\Psi_0\,, \tag{10}$$

which may also be derived by minimizing $E_e^{(2)}$ and $E_N^{(2)}$ with respect to $\delta\Psi_E$ and $\delta\Psi_N$, respectively. From Eqs. (9) and (10) it is easily seen that

$$
\begin{aligned}
\langle\delta\Psi_N|\mathcal{H}_E|\Psi_0\rangle &= \langle\delta\Psi_E|\mathcal{H}_N|\Psi_0\rangle\\
&= -\langle\delta\Psi_E|\mathcal{H}_0-E_0|\delta\Psi_N\rangle\,.
\end{aligned}
\tag{11}
$$

Hence, using Eq. (11), $E_{eN}^{(2)}$ reduces to

$$E_{eN}^{(2)}=2\langle\delta\Psi_E|\mathcal{H}_N|\Psi_0\rangle\,, \tag{12}$$

$$E_{eN}^{(2)}=2\langle\delta\Psi_N|\mathcal{H}_E|\Psi_0\rangle\,. \tag{13}$$

One could now apply this result to our problem of core polarization. For the perturbing Hamiltonian $\mathcal{H}_E$, we take the exchange potential at the position of the core electron due to the unpaired valence electron and for $\mathcal{H}_N$, the Fermi contact interaction due to the nuclear magnetic moment.

$$\mathcal{H}_E=-\frac{\psi_{\text{val}}(1)}{\psi_{\text{core}}(1)}\int\psi_{\text{val}}(2)\frac{e^2}{r_{12}}\psi_{\text{core}}(2)d\tau_2\,, \tag{14}$$

$$\mathcal{H}_N=\frac{16\pi}{3}\gamma_e\gamma_N\hbar^2\mathbf{I}\cdot\mathbf{S}\delta(\mathbf{r})\,. \tag{15}$$

In Eq. (15), γ_e is the magnetogyric ratio ($e/2$ Mc/sec) of the electron, γ_N is the magnetogyric ratio of the nucleus, and **I** and **S** are the respective spins of the nucleus and electron. Equation (14) requires some explanation[5]:

In the presence of an unpaired valence electron, with spin "up," Eq. (14) represents the difference in exchange potential seen by the up and down core electrons. If the restricted Hartree-Fock Hamiltonian for the core states were used as $\mathcal{H}_0$ in Eq. (9), we should consider two first-order equations of the type of Eq. (9), one for the up core state and one for the down. The equation for the up state would involve $+\mathcal{H}_E/2$ on the right and that for the down state $-\mathcal{H}_E/2$. For those effects which involve $\mathcal{H}_E$ to first order, one can consider the down state to remain unperturbed and the up state to be perturbed by $\mathcal{H}_E$ as given in Eq. (14).

Besides $E_{eN}^{(2)}$, the various higher order terms that could contribute to the hyperfine interaction are $\mathcal{H}_E^2\mathcal{H}_N$, $\mathcal{H}_E^3\mathcal{H}_N$, $\mathcal{H}_E^4\mathcal{H}_N$, $\cdots$. These terms are expected to be negligible in heavy atoms where $\mathcal{H}_E$ is a small perturbation compared to $\mathcal{H}_0$. For light atoms there may be a non-negligible contribution from such terms. We have not investigated its effect in lithium atom since our major interest is in Knight shift calculations. It will be shown in Sec. IV that these higher order terms in $\mathcal{H}_E$ do not have to be considered in core-polarization contributions to Knight shift. Higher order terms like $\mathcal{H}_N^2\mathcal{H}_E$, $\mathcal{H}_N^3\mathcal{H}_E$, $\cdots$, lead to terms in the energy nonlinear in nuclear spin and are of no interest to us.

For metal ψ_{val} becomes ψ_{cond}, the wave function for a conduction electron which extends over the entire crystal and therefore, involves more than one center. The perturbation equation for $\delta\Psi_E$ [Eq. (9)] cannot, therefore, be separated into radial and angular parts. Cohen, Goodings, and Heine[5] attempted to meet this limitation by expressing ψ_{cond} around the nucleus in question as a linear combination of spherical harmonics and used the linear independence of spherical harmonics of different orders to separate Eq. (9) into a number of independent differential equations. This procedure is rather cumbersome because one now has to solve a set of differential equations in place of Eq. (9). In the MP procedure, one considers the perturbations in the reverse order. This is justified because of the two alternative expressions (12) and (13) for $E_{eN}^{(2)}$. Instead of first considering the perturbation $\delta\Psi_E$ due to $\mathcal{H}_E$, let us consider the perturbation of the wave function $\delta\Psi_N$ due to $\mathcal{H}_N$. Thus, we can determine $\delta\Psi_N$ by solving Eq. (10) and obtain $E_{eN}^{(2)}$ from Eq. (13). Since $\mathcal{H}_N$ is a localized perturbation by a point source and ψ_0 refers to ψ_{core} (the wave function of the core electrons) which is, to a very good approximation, localized and centrosymmetric, Eq. (10) can be separated into radial and angular parts. It should be noted that when the wave function for the conduction electron is expanded as a sum of spherical harmonics, the MP method obviates the necessity of having to solve a set of differential equations; but instead, one has to evaluate a set of integrals arising out of Eq. (13). In principle, the two procedures for calculating $E_{eN}^{(2)}$ should lead to identical results; but in practice, this will not be exactly true. In the process of obtaining numerical solutions of the differential Eqs. (9) and (10), one weights various regions of space differently because of the different natures of the two perturbations $\mathcal{H}_E$ and $\mathcal{H}_N$. This point will become clear in Sec. III, where we compare our results with those of Cohen, Goodings, and Heine's EP calculations on lithium atom. We shall also show in Sec. III that for a model, where analytic solutions are obtainable with both EP and MP methods, the two methods do, in fact, lead to identical results.

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[18] T. P. Das and A. Mukherjee, J. Chem. Phys. **33**, 1808 (1960).

With these general remarks, we now proceed to the detailed forms of the equations that one has to solve for the MP method. Since, in a general case, one may have more than one core state to perturb, a formulation such as Dalgarno's for the perturbation of many-electron systems[19] is helpful. We will follow Dalgarno's method II (i.e., non-self-consistent perturbation) and obtain the first-order perturbation equations for $\delta\psi_N$ by minimizing the second-order energy [Eq. (59) in Dalgarno's paper] with respect to $\delta\psi_N$.

The first-order perturbation equations are then given by

$$(\mathcal{H}_i-\epsilon_i)\delta\psi_{i,N}-\sum_j (\epsilon_j-\epsilon_i)\langle\psi_j|\delta\psi_{i,N}\rangle\psi_j = -\mathcal{H}_N\psi_i+\sum_j \langle\psi_j|\mathcal{H}_N|\psi_i\rangle\psi_j, \quad (16)$$

where $\mathcal{H}_i$ is the one-electron Hamiltonian, and ψ_i, ψ_j are the one-electron wave functions in the Hartree-Fock approximation, and ϵ_i and ϵ_j are the corresponding eigenvalues. The first-order change in the wave function for the ith one-electron state due to $\mathcal{H}_N$ is $\delta\psi_{i,N}$. For a core ns state, Eq. (16) for $\delta\psi_{ns,N}$ takes the form

$$(\mathcal{H}_{ns}-\epsilon_{ns})\delta\psi_{ns,N}=\sum_{n's} (\epsilon_{n's}-\epsilon_{ns})\langle\psi_{n's}|\delta\psi_{ns,N}\rangle\psi_{n's} -\mathcal{H}_N\psi_{ns}+\sum_{n's} \langle\psi_{n's}|\mathcal{H}_N|\psi_{ns}\rangle\psi_{n's}. \quad (17)$$

One has to solve Eq. (17) for all occupied core ns states, since the s states are the only ones which do not have nodes at the origin and, hence, can contribute to the hyperfine interaction through the Fermi contact term. The summation terms on the right-hand side extend over all the core s states.

The zero-order one-electron wave function ψ_{ns} satisfies the equation

$$(\mathcal{H}_{ns}-\epsilon_{ns})\psi_{ns}=0. \quad (18)$$

That is, in atomic units

$$(-\nabla^2+V_{ns}-\epsilon_{ns})\psi_{ns}=0, \quad (19)$$

where V_{ns} is the one-electron potential seen by an electron in the ns state in the Hartree-Fock approximation. Therefore,

$$(V_{ns}-\epsilon_{ns})=\nabla^2\psi_{ns}/\psi_{ns}. \quad (20)$$

Substituting this in Eq. (17), we get

$$\left(-\nabla^2+\frac{\nabla^2\psi_{ns}}{\psi_{ns}}\right)\delta\psi_{ns,N} =\sum_{n's} (\epsilon_{n's}-\epsilon_{ns})\langle\psi_{n's}|\delta\psi_{ns,N}\rangle\psi_{n's} -\mathcal{H}_N\psi_{ns}+\sum_{n's} \langle\psi_{n's}|\mathcal{H}_N|\psi_{ns}\rangle\psi_{n's}. \quad (21)$$

If we now introduce the new function $\phi_{ns,N}$, defined by

$$\delta\psi_{ns,N}=-\frac{A}{4\pi}\frac{\psi_{ns}}{r}+\frac{\phi_{ns,N}}{r}Y_0{}^0(\theta,\phi), \quad (22)$$

where

$$A=\frac{16\pi}{3}\gamma_e\gamma_N\hbar^2I_z\frac{m}{a_0\hbar^2},$$

and remembering that $\nabla^2(1/r)=-4\pi\delta(\mathbf{r})$, Eq. (21) reduces to

$$-\frac{d^2\phi_{ns,N}}{dr^2}+\frac{A}{2\pi r^3}u_{ns}-\frac{A}{2\pi r^2}\frac{du_{ns}}{dr}+\frac{\phi_{ns,N}}{u_{ns}}\frac{d^2u_{ns}}{dr^2} =\sum_{n's} (\epsilon_{n's}-\epsilon_{ns})\{\langle u_{n's}|\phi_{ns,N}\rangle u_{n's}\} +A\sum_{n's} \psi_{n's}(0)\psi_{ns}(0)u_{n's}, \quad (23)$$

where we have used the notation

$$\psi_{ns}=[u_{ns}(r)/r]Y_0{}^0(\theta,\phi).$$

Because of the first term on the right-hand side, Eq. (23) is an integrodifferential equation and must be solved self-consistently. This term represents the influence of Pauli principle on the perturbed core states.

After determining $\delta\psi_{ns,N}$ by solving Eq. (23), one can get the second-order energy $E_{eN}{}^{(2)}$ using Eq. (13). Thus, substituting for the determinantal function $\delta\Psi_N$ in terms of the one-electron functions $\delta\psi_{ns,N}$ and using Eq. (14) for $\mathcal{H}_E$, we get

$$E_{eN}{}^{(2)}=2\sum_n \left\{\int\psi_{\mathrm{val}}(1)\delta\psi_{ns,N}(1)\psi_{\mathrm{val}}(2)\psi_{ns}(2) \times\frac{1}{r_{12}}d\tau_1d\tau_2-\sum_{n'}\int\psi_{\mathrm{val}}(1)\psi_{ns}(1)\psi_{\mathrm{val}}(2)\psi_{n's}(2) \times\frac{1}{r_{12}}d\tau_1d\tau_2\int\psi_{n's}\delta\psi_{ns,N}d\tau\right\}. \quad (24)$$

From this equation the correction a_c to the hyperfine constant a from core polarization is obtained by the equation

$$a_c=E_{eN}{}^{(2)}/IJ2\pi\hbar. \quad (25)$$

In solids and molecules, $\mathbf{J}$ is equal to the total spin $\mathbf{S}$; whereas, for atoms, $\mathbf{J}$ is the total angular momentum of the valence electrons.

III. RESULTS FOR LITHIUM ATOM $1s^22p$ AND $1s^22s$ STATES

For the lithium atom $1s^22p$ ($J=\frac{3}{2}$) state Eq. (23) for $\phi_{1s,N}$ takes the form

$$-\frac{d^2\phi_{1s,N}}{dr^2}+\frac{A}{2\pi r^3}u_{1s}-\frac{A}{2\pi r^2}\frac{du_{1s}}{dr}+\frac{\phi_{1s,N}}{u_{1s}}\frac{d^2u_{1s}}{dr^2} =A|\psi_{1s}(0)|^2u_{1s}. \quad (26)$$

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[19] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959).

To illustrate the nature of the solution of Eq. (26), we first assume a hydrogenic form for u_{1s} for which an exact solution of Eq. (23) can be obtained. The Coulson-Duncanson functions[20] represent such a choice.

$$\psi_{1s}=\left(\frac{z^3}{\pi}\right)^{1/2}e^{-zr},\quad \psi_{2p0}=\left(\frac{\xi^5}{\pi}\right)^{1/2}re^{-\xi r}\cos\theta \tag{27}$$

and

$$z=2.69,\quad \xi=0.525.$$

The solution of Eq. (21) is then found to be[21]

$$\phi_{1s,N}=\frac{A}{4\pi}(2z\ln r+2z^2r)u_{1s}(r)\,. \tag{28}$$

To find a solution $\delta\psi_{1s,N}$ which satisfies Eq. (5), we use the Schmidt orthogonalization procedure and obtain from Eqs. (22) and (28)

$$\delta\psi_{1s,N}=\frac{A}{4\pi}[F_{1s}-\langle\psi_{1s}|F_{1s}|\psi_{1s}\rangle]\psi_{1s}\,,$$

where (29)

$$F_{1s}=-\frac{1}{r}+2z\ln r+2z^2r\,.$$

From Eq. (14), the exchange perturbation $\mathcal{H}_E$ due to the $2p_0$ electron is given by

$$\mathcal{H}_E=-\frac{u_{2p}(r)}{3u_{1s}(r)}\left[\frac{1}{r^2}\int_0^r u_{2p}(s)u_{1s}(s)sds+r\int_r^\infty u_{2p}(s)u_{1s}(s)\frac{1}{s^2}ds\right]. \tag{30}$$

Hence, from Eqs. (24) and (30) it follows that

$$E_{eN}{}^{(2)}=-\tfrac{2}{3}B\left\{\int_0^\infty u_{2p}(r)\delta u_{1s,N}(r)dr\times\left[\frac{1}{r^2}\int_0^r u_{1s}(s)u_{2p}(s)sds+r\int_r^\infty u_{1s}(s)u_{2p}(s)\frac{1}{s^2}ds\right]\right\}, \tag{31}$$

where

$$B=\frac{A}{4\pi}\times\frac{e^2}{a_0}=\frac{4}{3}\frac{\gamma_N\gamma_e\hbar^2I_z}{a_0{}^3}\,,$$

and

$$\delta u_{1s,N}=\frac{4\pi}{A}r\delta\psi_{1s,N}\,. \tag{32}$$

For the Coulson-Duncanson functions using Eqs. (27), (28), and (31), and performing the necessary integrations, we get

$$E_{eN}{}^{(2)}=-\frac{32}{9}B\xi^5z^3\left[\frac{147z^2}{4(z+\xi)^8}-\frac{15}{8(z+\xi)^6}-\frac{273z}{8(z+\xi)^7}-\frac{21z\ln(z+\xi)}{2(z+\xi)^7}+\frac{48z\ln2}{(z+\xi)^7}+\frac{21z\ln z}{2(z+\xi)^7}\right]. \tag{33}$$

Substituting the values of z and ξ, one gets

$$E_{eN}{}^{(2)}=-0.0540B\,. \tag{34}$$

From Eqs. (25) and (32), remembering $I=J=\frac{3}{2}$, it then follows that

$$a_c=\frac{4\mu_N\mu_0E_{eN}{}^{(2)}}{3a_0{}^3IJ(2\pi\hbar)B}=-5.24\ \text{Mc/sec}\,, \tag{35}$$

where $\mu_N=\gamma_NI\hbar$ is the magnetic moment of the Li^7 nucleus and μ_0 is the Bohr magneton.

Since $u_{1s}(r)$ involves a single exponential for the Coulson-Duncanson function, one can obtain an exact analytic solution for the perturbation equation (16) for the EP method, with $\delta\psi_{iN}$ and $\mathcal{H}_N$ replaced by $\delta\psi_{iE}$ and $\mathcal{H}_E$, respectively.

$$\delta\psi_{1s,E}=\frac{8}{9}\left(\frac{z^3}{\pi}\right)^{1/2}\frac{\xi^5e^{-zr}}{(z+\xi)^7}\left\{\frac{3(z+\xi)^4r^2e^{-2\xi r}}{4\xi}+\left[\frac{3(z+\xi)^4}{4\xi^2}+\frac{9(z+\xi)^3}{2\xi}\right]re^{-2\xi r}+\left[\frac{3(z+\xi)^4}{8\xi^3}+\frac{9(z+\xi)^3}{4\xi^2}+\frac{51(z+\xi)^2}{4\xi}\right]e^{-2\xi r}+\frac{75e^{-2\xi r}}{4r}-\frac{24e^{(z-\xi)r}}{r}-\frac{75z}{2}\int\frac{e^{-2\xi r}}{r}dr+48z\int\frac{e^{(z-\xi)r}}{r}dr\right\}-\frac{28}{3}\left(\frac{z^3}{\pi}\right)^{1/2}\frac{z^2\xi^5e^{-zr}}{(z+\xi)^7}\left(r+\frac{1}{z}\ln r-\frac{1}{2z^2r}\right). \tag{36}$$

Substituting $\delta\psi_{1s,E}$ from Eq. (36) into Eq. (12), one obtains, after some manipulation, exactly the same expression for $E_{eN}{}^{(2)}$ as in Eq. (33).

The value of a_c in Eq. (35) is about one-half of Goodings's[4] calculated value (−10.7 Mc/sec) by the SP method and is in somewhat better agreement with Cohen, Goodings, and Heine's[5] value (−8.5 Mc/sec) by the EP method. However, one does not expect very good agreement with these earlier results because the single-exponential hydrogen functions are not good approximations to the Hartree-Fock wave functions.[22]

To get a result by the MP method which could be properly compared in terms of accuracy with Cohen,

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[20] C. Coulson and W. E. Duncanson, Proc. Roy. Soc. (Edinburgh) **62**, 37 (1944).

[21] C. Schwartz, Ann. Phys. (N. Y.) **6**, 156 (1959).

[22] Per-Olov Löwdin and K. Appel, Phys. Rev. **103**, 1746 (1956).

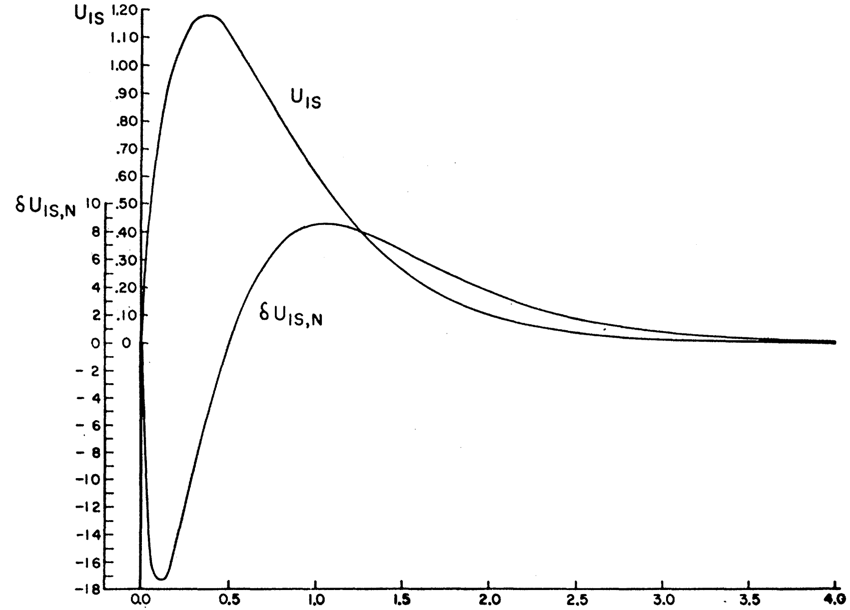

FIG. 1. Plot of unperturbed (u_{1s}) wave function and first-order perturbation $\delta u_{1s,N}$ as function of r for lithium atom $1s^22p$ configuration.

Goodings, and Heine's EP calculation and Goodings' SP calculation, we next solved Eq. (23) using Hartree-Fock wave functions. The solution has now to be obtained by numerical integration of Eq. (23). In Fig. 1, the function $\delta u_{1s,N}$ [defined in Eq. (32)] is plotted, together with Goodings' Hartree-Fock wave function[20] u_{1s}, which was employed in our calculations. The function $\delta u_{1s,N}$ resembles a $2s$ type function, in that, it has a node, but $\delta\psi_{1s,N}=(A/4\pi)(\delta u_{1s,N}/r)$ goes to negative infinity at the origin.

Using Eq. (31), together with Goodings' HF wave functions u_{1s}, u_{2p}, and $\delta u_{1s,N}$ of Fig. 1, it follows that

$$E_{eN}^{(2)}=-\tfrac{2}{3}B(0.137). \tag{37}$$

From Eq. (25) this leads to

$$a_c=-8.9\text{ Mc/sec}. \tag{38}$$

This value compares very favorably with Cohen, Goodings, and Heine's EP value (Table I). This is satisfying in light of our Eqs. (12) and (13) and our earlier demonstration that EP and MP methods lead to identical results whenever exact solutions of Eqs. (9) and (10) are obtainable.

Both ours and Cohen, Goodings, and Heine's values for a_c are in slight disagreement with Goodings' value (Table I) obtained by the SP method. However, no measured value of a_c is available, so it is rather difficult to assess the importance of this small disagreement between the values obtained by MP (and EP) and SP methods.

The feasibility and accuracy of the MP method has now been demonstrated by its favorable comparison with the results of the EP method for the lithium atom $1s^22p$ state. We would next like to show the flexibility of the MP method by a consideration of core polarization effects for the $1s^22s$ state of lithium atom. The perturbation equation to be solved to get $\delta\psi_{1s,N}$ (or $\phi_{1s,N}$) in this case is exactly the same as in Eq. (26) except that u_{1s} may be different from its value for the $1s^22p$ state. Available tables[23] of u_{1s} for $1s^22s$ and $1s^22p$ states show that there is only a very slight difference between the values of u_{1s} in the two cases. One could

TABLE I. List of contributions to hyperfine constants in Mc/sec for lithium atom $1s^22s$ and $1s^22p$ states.

	$1s^22s$			$1s^22p$		
	Core polarization	Direct $2s$ contribution	Total	Core polarization	Direct $2p$ contribution	Total
Goodings	106	284	390	−10.7	0	−10.7
Cohen, Goodings, and Heine[a]	86.74	286.26	373.0	−8.5	0	−8.5
This paper	83.76	284	367.76	−8.9	0	−8.9
Experimental			401.786			

[a] The direct $2s$ contribution is taken from Table I of Ref. 5.

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[23] D. A. Goodings, Ph.D. thesis, Cambridge University, Cambridge, England, 1961 (unpublished).

therefore use the same $\phi_{1s,N}$ for both $1s^22p$ and $1s^22s$ states. If using this approximation we find good agreement with results obtained by Cohen, Goodings, and Heine's EP calculation (which is not subject to the same approximation), we can indeed justify our claim about the flexibility of the MP method. For heavier atoms, the alteration in core wave functions u_{ns} for different atomic configurations would be even less than for lithium; and so the flexibility approximation will be more justified.

The second-order energy expression $E_{eN}^{(2)}$ for the lithium atom $1s^22s$ state is then given by

$$E_{eN}^{(2)}=-2B\left\{\int_0^\infty u_{2s}(r)\delta u_{1s,N}(r)\times\left[\frac{1}{r}\int_0^r u_{1s}(s)u_{2s}(s)ds+\int_r^\infty u_{1s}(s)u_{2s}(s)\frac{1}{s}ds\right]dr\right\}. \tag{39}$$

On evaluating the integrals in Eq. (39), one gets $E_{eN}^{(2)}=2B(0.1434)$. The hyperfine constant is therefore

$$a_c=83.76\ \text{Mc/sec}. \tag{40}$$

The comparison of this value with Cohen, Goodings, and Heine's and Goodings' values (Table I) is very satisfying.

IV. CORE CONTRIBUTION TO KNIGHT SHIFT IN LITHIUM METAL

As another important application of the MP method, we shall consider the magnetic field produced at the Li^7 nucleus in lithium metal as a result of the exchange polarization of the core $1s$ electrons when the conduction electrons are polarized by the external magnetic field. The usual expression for the Knight shift due to the conduction electrons is given by[24]

$$\frac{\Delta H}{H}=\frac{8\pi}{3}\chi_p\langle|\psi_F(0)|^2\rangle_{\text{av}}, \tag{41}$$

where χ_p is the spin susceptibility per atom, and $\langle|\psi_F(0)|^2\rangle_{\text{av}}$ is the average electron density at the nucleus from electrons at the Fermi surface. Equation (41) can be interpreted in the following way: Of the conduction electrons near the Fermi surface, a fraction $(\frac{1}{2}+\chi_pH/2\mu_0)$ have their spins parallel to the field, and a fraction $(\frac{1}{2}-\chi_pH/2\mu_0)$ have their spins antiparallel to the field. When these electrons interact with the nuclear moment through the interaction term $\mathcal{H}_N$, we get the effective field ΔH in Eq. (41) out of the difference in populations in the parallel and antiparallel spin states. This population difference between the parallel and antiparallel conduction electron states also leads to an exchange polarization potential to the core electrons, given by

$$\mathcal{H}_E=-\frac{\chi_pH}{\mu_0}\frac{\psi_k(1)}{\psi_{\text{core}}(1)}\int\psi_k(2)\frac{1}{r_{12}}\psi_{\text{core}}(2)d\tau_2. \tag{42}$$

It is this potential $\mathcal{H}_E$ which enables the core electrons to produce an additional field at the nucleus.

Since $\mathcal{H}_E$ is now a weaker perturbation than in Eq. (14) by a factor χ_pH/μ_0, the perturbation methods EP and MP are more justified than in atoms. Also, it is clear from Eq. (42) that terms of the order $\mathcal{H}_E{}^2\mathcal{H}_N$, $\mathcal{H}_E{}^3\mathcal{H}_N$, $\cdots$, would lead to contributions to the Knight shift which are proportional, respectively, to the first, second, and higher powers of the field. However, there is little current evidence for such contributions to the Knight shifts in metals.

To calculate the contribution to the Knight shift from the core $1s$ electrons by the MP method, we then proceed in the same manner as in Sec. III to calculate $E_{eN}^{(2)}$ as given by Eq. (13). For the perturbed core wave function, the function $\delta u_{1s,N}$ (Fig. 1) for the atomic lithium $1s^22p$ state was used. This is again an approximation because there may be a small difference between the wave functions u_{1s} for the metal, and for the atomic $1s^22p$ state. However, our experience with the lithium atom $1s^22s$ state in Sec. III indicates that the error due to this approximation has little effect on $E_{eN}^{(2)}$. We would also like to point out that this error would be expected to be smaller for the metal than for the $1s^22s$ atomic state because the conduction electron wave functions appear to have predominantly p character at the Fermi surface.[17]

Making use of Eqs. (13), (25), and (42), and remembering that we have to average over the Fermi surface in calculating Knight shifts, we get

$$\frac{\Delta H}{H}=\frac{8\pi}{3}\chi_p\frac{2}{A_F}\left\langle\int_0^{r_s}\psi_{k_F}(1)\delta\psi_{1s,N}(1)\times\psi_{k_F}{}^*(2)\psi_{1s}(2)\frac{1}{r_{12}}d\tau_1d\tau_2\right\rangle_{\text{Fermi surface}}, \tag{43}$$

where ψ_{k_F} is the wave function for a conduction electron at the Fermi surface, r_s is the radius of the Wigner-Seitz sphere, and A_F is the area of the Fermi surface. Equation (43) can be evaluated using available wave functions ψ_{k_F} for lithium metal. Of the published wave functions for lithium, those which are available in a readily usable form are the recent ones by Kohn and Callaway.[17]

$$\psi_k=\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(N)^{1/2}}\left[u_0(r)+iku_1(r)P_1(\cos\theta_{kr})+k^2(u_2(r)P_2(\cos\theta_{kr})+\phi(r))\right]. \tag{44}$$

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[24] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

The potential used in obtaining these results was an empirical potential which is expected to be more accurate than a calculated potential based on some model. In Eq. (44), θ_{kr} is the angle between a radius vector $\mathbf{r}$ and wave vector $\mathbf{k}$. The functions $u_0(r)$, $\phi(r)$, $u_1(r)$, and $u_2(r)$ were given in tabulated form and N is a normalization factor calculated up to k_F^2 term (where k_F is the Fermi momentum in the spherical Fermi surface approximation).

$$N=4\pi(1+2.79333k_F^2)\,. \tag{45}$$

Since the Fermi surface in lithium approximates a sphere quite closely, we can take the magnitude of $\mathbf{k}_F$ in all directions as the same. The details of the calculations for evaluating the integral in Eq. (43) are given in the Appendix. It is shown there that including up to terms of order k_F^2 [Eq. (A4)]

$$\begin{aligned}\psi_{k_F}(r)&=As(k_F,r)P_0(\cos\theta_{kr})+Ap(k_F,r)P_1(\cos\theta_{kr})\\&\quad+Ad(k_F,r)P_2(\cos\theta_{kr})\,,\\ As(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\bigg[j_0(k_F,r)u_0(r)-k_Fj_1(k_F,r)u_1(r)\\&\quad+k_F^2\bigg(j_0(k_F,r)\phi(r)-j_2(k_F,r)u_2(r)\\&\quad-\frac{2.79333}{2}j_0(k_F,r)u_0(r)\bigg)\bigg]\,,\\ Ap(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\bigg[3u_0j_1+k_F(j_0u_1-2j_2u_1)\\&\quad+k_F^2\bigg(1.2j_1u_2+3j_1\phi-1.8j_3u_2\\&\quad-\frac{3(2.79333)}{2}u_0j_1\bigg)\bigg]\,,\\ Ad(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\bigg[-5j_2u_0+k_F(3j_3u_1-2j_1u_1)\\&\quad+k_F^2\bigg(j_0u_2-\frac{10}{7}j_2u_2-5j_2\phi+\frac{18}{7}j_4u_2\\&\quad+\frac{5(2.79333)}{2}j_2u_0\bigg)\bigg]\,,\end{aligned}\tag{46}$$

where $j_n(k_F,r)$ is the spherical Bessel function of the order n. Using Eq. (46), it is shown in the Appendix [Eq. (A15)], that one obtains after some manipulation

$$\begin{aligned}\frac{\Delta H}{H}&=\frac{8\pi\chi_p}{3}\frac{1}{2\pi}\int\delta\psi_{1s,N}(r_1)\psi_{1s}(r_2)\\&\quad\times\bigg\{(4\pi)^3\frac{As(k_F,r_1)As^*(k_F,r_2)}{r_>}\\&\quad+3\left(\frac{4\pi}{3}\right)^3Ap(k_F,r_1)Ap^*(k_F,r_2)\frac{r_<}{r_>^2}\\&\quad+5\left(\frac{4\pi}{5}\right)^3Ad(k_F,r_1)Ad^*(k_F,r_2)\frac{r_<^2}{r_>^3}\bigg\}r_2^2dr_2r_1^2dr_1\,.\end{aligned}\tag{47}$$

The contributions to $\Delta H/H$ from the three terms in Eq. (47) involving As, Ap, and Ad refer, respectively, to the s, p, and d parts of the conduction electron wave function at the Fermi surface. These were evaluated by numerical integration and are listed in Table II. It can be seen that $(\Delta H/H)_{cp}$ is almost equal to $(\Delta H/H)_{cs}$ but opposite in sign. In contrast, $(\Delta H/H)_{cd}$ is about a factor of 25 smaller than both $(\Delta H/H)_{cp}$ and $(\Delta H/H)_{cs}$. This leads us to expect that the contributions to the core polarization from f and higher angular momentum parts of the conduction electron wave function would be negligible. Unfortunately, it is not possible to test this point using Callaway and Kohn's wave function, because they did not give higher angular momentum components beyond d. The value of the total core contribution, $(\Delta H/H)_c$ in units of $(647.5\ \chi_p)$, namely -0.00544, is to be compared with the value of 0.10280 in the same units, for $(\Delta H/H)_{\mathrm{direct}}$ that one gets using Kohn and Callaway's wave functions and Eq. (41). So we find that the core polarization contributes about -5.3% correction to the Knight shift. Also it is to be noted that, while the s character of the conduction electron wave function is alone important, for the direct contribution to the Knight shift as given by Eq. (41), the core polarization depends sensitively on the s and p parts of the wave function, since there is a near cancellation between $(\Delta H/H)_{cs}$ and $(\Delta H/H)_{cp}$. It is therefore imperative to know accurately the relative amounts of s and p characters in the wave functions for other metals, since the core-polarization contribution may be a more significant fraction of the direct contribution. This point has also been noted by Cohen, Goodings, and Heine.[5] These authors assumed that the conduction electron wave function can be well approximated by a combination of $2s$ and $2p$ atomic functions. In such a case, the core polarization can be calculated by taking a weighted combination of the core polarizations for atomic $1s^22s$ and $1s^22p$ configurations. However, in Figs. 2 and 3, we have compared As and Ap with the $2s$ and $2p$ atomic wave functions, respectively, obtained by Goodings.[4] It is seen that, while there is a reasonable

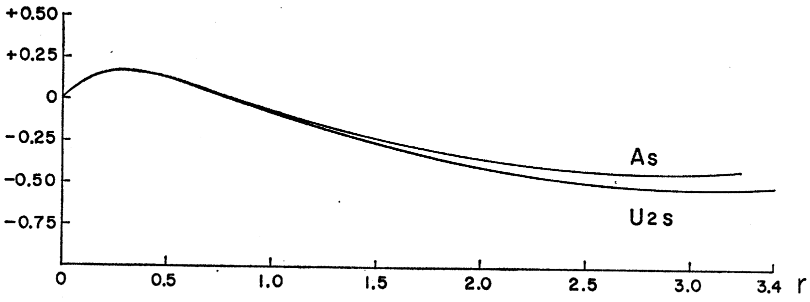

FIG. 2. Comparison of the s part of the conduction electron wave function (at Fermi surface) with Goodings' $2s$ wave function (u_{2s}) for lithium atom $1s^22p$ configuration.

similarity in shapes between the metallic and atomic wave functions, the correspondence is far from exact. To make a quantitative application of the EP method comparable to our MP calculations, one would have to solve two equations of the type of Eq. (9) using Eq. (42) for $\mathcal{H}_E$ and then calculate $(\Delta H/H)_c$ using Eq. (12). With the MP method, however, because of the flexibility in using $\delta\psi_{1s,N}$ as long as the core wave functions do not vary substantially, we did not have to solve any new differential equations to obtain $(\Delta H/H)_c$. This is an illustration of the computational advantage of the MP method.

In our numerical calculations leading to the results in Table II, we had to make use of the expressions in Eq. (46) correct to k_F^2. This was necessary because of the form of Eq. (44) in which Callaway and Kohn's wave function was available. However, Eq. (47) can be used for any general wave function (such as orthogonalized plane wave and augmented plane wave), since one can obtain As, Ap, and Ad by expanding the conduction electron wave function in spherical harmonics.

TABLE II. List of contributions to Knight shift in lithium metal.

Contributions[a] to $\Delta H/H$	Value
Core-polarization s part, $(\Delta H/H)_{cs}$	0.02355
Core-polarization p part, $(\Delta H/H)_{cp}$	−0.02813
Core-polarization d part, $(\Delta H/H)_{cd}$	−0.00085
Total core polarization $(\Delta H/H)_c$	−0.00544
Direct contribution[b] $(\Delta H/H)_{\text{direct}}$	0.10280
Grand total $(\Delta H/H)_{\text{total}}$	0.09736
Experiment[c]	0.101

[a] The tabulated numbers are in units of a_0^{-3} (atomic units). To correct to the usual dimensionless manner (%) that Knight shift data are obtained, multiply by 647.5 χ_p, where χ_p is the spin susceptibility per gram.
[b] Calculated using Kohn and Callaway's wave function (Ref. 17).
[c] Taken from Table IV, Ref. 24.

CONCLUSION

As we mentioned at the outset, our motivation in developing the MP method was to find a procedure for investigating the contribution from exchange polarization to Knight shifts in metals and alloys. While the EP method as developed by Cohen, Goodings, and and Heine can, in principle, be applied in any situation, one would like to have a method that is computationally simpler and flexible enough to apply for a nucleus in a variety of environments. Our experience with lithium nucleus in the three situations discussed here leads us to believe that the MP method can be extended to give reliable results in other cases. The necessity for careful investigations of core polarizations is strongly felt at the present time, because a variety of Knight shift data in metals, alloys, and internal fields in ferromagnets, are now available; and it appears that direct contributions from conduction electrons cannot quantitatively explain such data.

We would like to conclude by making a few comments on the self-consistency problem in core-polarization calculations in general and specifically as pertinent to the MP method. In an atom containing an unpaired electron, the many-electron wave function has to be

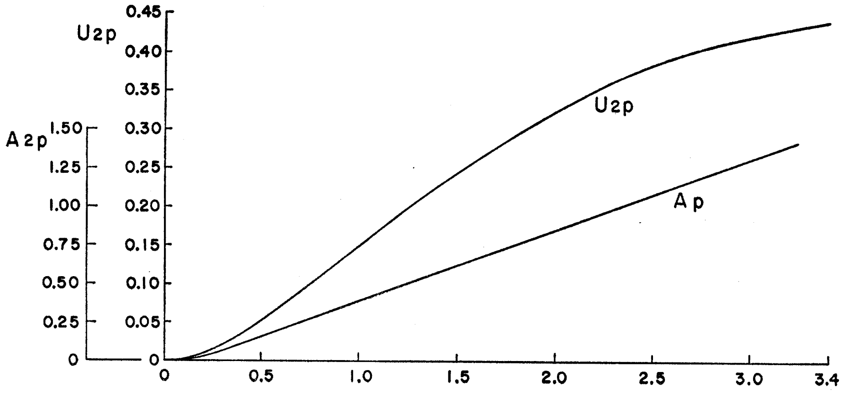

FIG. 3. Comparison of the p part of the conduction electron wave function (at Fermi surface) with Goodings' $2p$ wave function (u_{2p}) for lithium atom $1s^22p$ configuration.

an eigenfunction of $\mathbf{S}^2$. As has been pointed out by a number of authors, in a correct application of the Hartree-Fock method, this condition must be built in as a constraint. This is the case with the PSP method. The SP method, however, does not have this constraint, and the results from both SP or SPP methods are therefore somewhat suspect. Heine has pointed out that it is the self-consistency procedure in the SP method which is responsible for its dangers because it leads to an uncertain admixture of correlation and exchange effects and may in fact overemphasize the correlation unduly. The EP method, which considers the exchange polarization as a perturbation and has no self-consistency built in, is free from this danger although it is evidently less accurate than PSP. In the MP method, however, the perturbed state is not an eigenfunction of $\mathbf{S}^2$ because of the nature of $\mathcal{H}_N$; hence, there is no condition of constraint regarding the total spin. Self-consistency can therefore be used in the MP method without any fear of spurious contributions from correlation. However, our aim was to extend this method to metals where self-consistency is rather difficult to apply even for restricted Hartree-Fock calculations. We have therefore not explored the effects of self-consistency (Dalgarnos' method I) here.

ACKNOWLEDGMENTS

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APPENDIX

From Eq. (24), the second-order change in energy due to the exchange polarization of the core electrons by the conduction electrons at the Fermi surface is

$$E_{eN}^{(2)}=-\frac{2}{4\pi k_F^2}\left\langle\int_0^{r_s}\psi_{k_F}(1)\delta\psi_{1s,N}(1)\times\psi_{k_F}^*(2)\psi_{1s}(2)\frac{1}{r_{12}}d\tau_1 d\tau_2\right\rangle_{\text{Fermi surface}},\quad\text{(A1)}$$

where r_s is the radius of the Wigner, Seitz sphere $=3.21$ a_0, k_F is the Fermi momentum $=0.59788/a_0$, and

$$\psi_{k_F}=\frac{e^{i\mathbf{k}_F\cdot\mathbf{r}}}{(N)^{1/2}}\left[u_0(r)+ik_F u_1(r)P_1(\theta_{kr})+k_F^2(u_2(r)P_2(\theta_{kr})+\phi(r))\right],\quad\text{(A2)}$$

θ_{kr} being the angle between $\mathbf{k}_F$ and $\mathbf{r}$, and N the normalization factor, $4\pi(1+2.79333k_F^2)$ and for abbreviation we denote $P_l(\cos\theta_{kr})$ by $P_{l(\theta_{kr})}$ where θ_{kr} is the angle between $\mathbf{k}_F$ and $\mathbf{r}$. On expanding $e^{i\mathbf{k}_F\cdot\mathbf{r}}$ and N, and keeping terms up to k_F^2, ψ_{k_F} can be written as

$$\psi_{k_F}(r)=As(k_F,r)P_0(\theta_{kr})+Ap(k_F,r)P_1(\theta_{kr})+Ad(k_F,r)P_2(\theta_{kr}),\quad\text{(A3)}$$

where

$$\begin{aligned}As(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\Bigg[j_0(k_F,r)u_0(r)-k_F j_1(k_F,r)u_1(r)\\&\quad+k_F^2\bigg(j_0(k_F,r)\phi(r)-j_2(k_F,r)u_2(r)-\frac{2.79333}{2}j_0(k_F,r)u_0(r)\bigg)\Bigg],\\Ap(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\Bigg[3j_1u_0+k_F(j_0u_1-2j_2u_1)\\&\quad+k_F^2\bigg(1.2j_1u_2+3j_1\phi-1.8j_3u_2-\tfrac{3}{2}(2.79333)u_0j_1\bigg)\Bigg],\\Ad(k_F,r)&=\frac{1}{(4\pi)^{1/2}}\Bigg[-5j_2u_0+k_F(3j_3u_1-2j_1u_1)\\&\quad+k_F^2\bigg(j_0u_2-\frac{10}{7}j_2u_2-5j_2\phi+\frac{18}{7}j_4u_2+\tfrac{5}{2}(2.79333)u_0j_2\bigg)\Bigg],\end{aligned}\quad\text{(A4)}$$

where $j_n(k_F,r)$ is the spherical Bessel function of order n. Using Eqs. (A3) and (A4), Eq. (A1) takes the form

$$\begin{aligned}E_{eN}^{(2)}=-\frac{1}{2\pi}\int\delta\psi_{1s,N}(r_1)\psi_{1s}(r_2)\frac{1}{r_{12}}\{&[As(k_F,r_1)+Ap(k_F,r_1)P_1(\theta_{k1})+Ad(k_F,r_1)P_2(\theta_{k1})]\\&\times[As^*(k_F,r_2)+Ap^*(k_F,r_2)P_1(\theta_{k2})\\&+Ad^*(k_F,r_2)P_2(\theta_{k2})]\}d\tau_1 d\tau_2\sin^2\theta_{k_F}d\theta_{k_F}d\phi_{k_F},\end{aligned}\quad\text{(A5)}$$

θ_{k1} representing the angle between $\mathbf{k}_F$ and $\mathbf{r}_1$ and θ_{k2} the angle between $\mathbf{k}_F$ and $\mathbf{r}_2$. We perform the integration over the spherical Fermi surface first, and then integrate out the angular parts of $d\tau_1$ and $d\tau_2$.

Since the directions of $\mathbf{r}_1$ and $\mathbf{r}_2$ are arbitrary, let $\mathbf{r}_1$ be directed along $\mathbf{k}_z$ for convenience. Using the addition theorem for spherical harmonics

$$\begin{aligned}P_2(\theta_{k2})&=\frac{4\pi}{5}\sum_{m=-2}^{2}Y_2^{m*}(\theta_{k1},\phi_{k1})Y_2^m(\theta_{12},\phi_{12}),\\P_1(\theta_{k2})&=\frac{4\pi}{3}\sum_{m=-1}^{1}Y_1^{m*}(\theta_{k1},\phi_{k1})Y_1^m(\theta_{12},\phi_{12}),\end{aligned}\quad\text{(A6)}$$

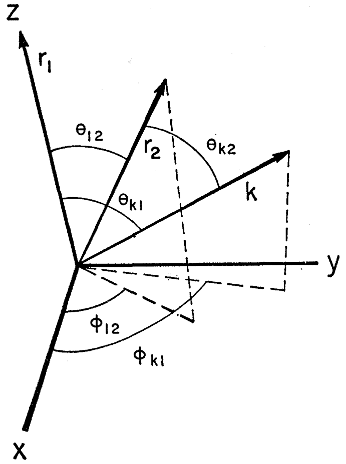

FIG. 4. Relative orientations of **k**, $\mathbf{r}_1$, and $\mathbf{r}_2$.

one can evaluate the following integrals over the Fermi surface:

$$\frac{4\pi}{3}\int P_1(\theta_{k1})\sum_{m=-1}^{1} Y_1^{m*}(\theta_{k1},\phi_{k1})Y_1^m(\theta_{12},\phi_{12})d\Omega_k = \frac{4\pi}{3}P_1(\theta_{12})\delta_{m0}, \quad \text{(A7)}$$

$$\frac{4\pi}{5}\int P_2(\theta_{k1})\sum_{m=-2}^{2} Y_2^{m*}(\theta_{k1},\phi_{k1})Y_2^m(\theta_{12},\phi_{12})d\Omega_k = \frac{4\pi}{5}P_2(\theta_{12})\delta_{m0}, \quad \text{(A8)}$$

$$\int P_j(\theta_{k1})P_i(\theta_{k2})d\Omega_k = 0, \quad i\neq j.$$

Equation (A5) then reduces to

$$E_{eN}^{(2)} = -\frac{1}{2\pi}\int \delta\psi_{1s,N}(r_1)\psi_{1s}(r_2)\frac{1}{r_{12}}\bigg[4\pi As(k_F,r_1) \times As^*(k_F,r_2)+\frac{4\pi}{3}Ap(k_F,r_1)Ap^*(k_F,r_2)P_1(\theta_{12}) +\frac{4\pi}{5}Ad(k_F,r_1)Ad^*(k_F,r_2)P_2(\theta_{12})\bigg]d\tau_1 d\tau_2. \quad \text{(A9)}$$

In order to perform the angular integration involved in Eq. (A9) the following relationships will be used:

$$\frac{1}{r_{12}} = 4\pi\sum_{l=0}^{\infty}\frac{1}{(2l+1)}\frac{r_<^l}{r_>^{l+1}}\sum_{m=-l}^{l} Y_l^{m*}(\theta_1,\phi_1) \times Y_l^m(\theta_2,\phi_2), \quad \text{(A10)}$$

$$P_1(\theta_{12}) = \frac{4\pi}{3}\sum_{m=-1}^{1} Y_1^{m*}(\theta_1,\phi_1)Y_1^m(\theta_2,\phi_2),$$

$$P_2(\theta_{12}) = \frac{4\pi}{5}\sum_{m=-2}^{2} Y_2^{m*}(\theta_1,\phi_1)Y_2^m(\theta_2,\phi_2), \quad \text{(A11)}$$

where (A11) again follows from the spherical harmonic addition theorem. Thus,

$$\int \frac{1}{r_{12}}P_1(\theta_{12})d\Omega_1 d\Omega_2 = \frac{(4\pi)^2}{3}\sum_{l=0}^{\infty}\frac{1}{(2l+1)}\frac{r_<^l}{r_>^{l+1}} \times\sum_{m'=-l}^{l}\int Y_l^{m'*}(\theta_1,\phi_1)Y_l^{m'}(\theta_2,\phi_2) \times\sum_{m=-1}^{1} Y_1^m(\theta_1,\phi_1)Y_1^{m*}(\theta_2,\phi_2)d\Omega_1 d\Omega_2 = \left(\frac{4\pi}{3}\right)^2\frac{r_<}{r_>^2}\times 3. \quad \text{(A12)}$$

$$\int \frac{1}{r_{12}}P_2(\theta_{12})d\Omega_1 d\Omega_2 = \left(\frac{4\pi}{5}\right)^2\frac{r_<^2}{r_>^3}\times 5, \quad \text{(A13)}$$

$$\int \frac{1}{r_{12}}P_0(\theta_{12})d\Omega_1 d\Omega_2 = (4\pi)^2\frac{1}{r_>}. \quad \text{(A14)}$$

The final expression for $E_{eN}^{(2)}$ is then

$$E_{eN}^{(2)} = -\frac{1}{2\pi}\int \delta\psi_{1s,N}(r_1)\psi_{1s}(r_2) \times\{(4\pi)^2 As(k_F,r_1)As^*(k_F,r_2)(1/r_>) +3(4\pi/3)^3 Ap^*(k_F,r_2)Ap(k_F,r_1)(r_</r_>^2) +5(4\pi/5)^3 Ad(k_F,r_1)Ad^*(k_F,r_2)(r_<^2/r_>^3)\} \times r_2^2 dr_2 r_1^2 dr_2, \quad \text{(A15)}$$

which involves only radial integrations over r_1 and r_2.