

its Knight shift and T_1 are concerned, the Knight shift of magnesium being $+0.111\%$,³² so that it appears that in this case the direct-contact contribution K_s to the total Knight shift is substantial and dominant. The Fermi surface of beryllium differs from that of magnesium in the important aspect that the third-zone "lens" figure at Γ enclosing electrons in magnesium³¹ is completely absent in beryllium.⁹ Correspondingly, the energy of the Γ_4^- representation in beryllium lies above the Fermi energy, whereas in magnesium it lies below. The relatively large positive direct-contact contribution calculated by Shyu *et al.*,⁸ is based on the Γ_4^- representation. By contrast, the state H_1 (near the "cigars") gives a small negative shift.⁸ It would appear⁹ that the Fermi surface in beryllium is mainly in the vicinity of the symmetry points H , K , and M . All of these points probably have very little s character, so that the predominantly non- s character of the Knight shift and relaxation time appear qualitatively plausible.

³² T. J. Rowland, in *Progress in Material Science*, edited by Bruce Chalmers (Pergamon Press, Inc., New York, 1961), Vol. IX, p. 14.

The fact that the quadrupole coupling in beryllium, even though larger than Knight's value by 25%, is still smaller than the theoretical estimate based on the lattice contribution to the field gradient and a new independent value of the quadrupole moment is indeed surprising. It indicates that the conduction-electron contribution to the gradient opposes that due to the lattice of point charges. In view of the appreciable p -like character of the conduction-electron wave function at the Fermi surface, deduced from the Knight shift and T_1 results, a substantial conduction-electron contribution to the field gradient may be reasonable.

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Exchange Potential for Nearly Free Electrons

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The approximation of the exchange potential which varies as the cube root of the density is examined. The optimum value of the coefficient in this expression, i.e., the value which minimizes the total energy of the system, is determined for a sinusoidal perturbation upon a system of free electrons as a function of the wavelength of the perturbation. For very long waves the coefficient assumes the value proposed by Gaspar. However, over a range of wavelengths which, in relation to the Fermi energy, are more appropriate for conduction electrons in a metal, the coefficient increases, well beyond Slater's original value, and then experiences a fairly sharp cutoff. Beyond this range the coefficient tends to vanish for decreasing wavelengths. A higher-order approximation incorporating this characteristic is also presented.

THE Hamiltonian for a system of $2N$ electrons,

$$\mathcal{H} = -\sum_{i=1}^{2N} [\nabla_i^2 - w(\mathbf{r}_i) - q \sum_{j=i+1}^{2N} r_{ij}^{-1}],$$

where w arises from external forces, $q = 2me^2/\hbar^2$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, assumes in the one-particle—or Hartree-Fock—approximation the form

$$\mathcal{H}_0 = \sum_{i=1}^{2N} H(\mathbf{r}_i),$$

whereupon the total wave function Ψ for the system in the ground state becomes the Slater determinant constructed from the N solutions with the lowest eigen-

values ϵ_n of the equation

$$H\psi_n = \epsilon_n\psi_n. \quad (1)$$

The total energy of the system is found from $E = \langle \Psi | \mathcal{H} | \Psi \rangle$.

Substituting for the exchange operator the function $A(\mathbf{r})$ proposed by Slater¹ gives

$$H(\mathbf{r}_1) = -\nabla_1^2 + w(\mathbf{r}_1) + 2q \int d\mathbf{r}_2 \rho(\mathbf{r}_2) r_{12}^{-1} - A(\mathbf{r}_1), \quad (2)$$

where, with respect to

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{n=1}^N \psi_n^*(\mathbf{r}_1) \psi_n(\mathbf{r}_2), \quad (3)$$

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}),$$

¹ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

and

$$A(\mathbf{r}_1) = q\rho^{-1}(\mathbf{r}_1) \int d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1) r_{12}^{-1}. \quad (4)$$

A further simplification of the exchange potential employs free-electron wave functions in Eq. (3), whence Eq. (4) yields

$$A_0(\mathbf{r}) = (6/\pi)^{1/3} q \gamma \rho^{1/3}(\mathbf{r}), \quad (5)$$

where, in this instance, $\gamma = \frac{3}{2}$. Such approximations are commonly welcome where the influence of the exchange operator on the wave function is incommensurate with its complexity.

Gaspar² has contended, as have Kohn and Sham³ after a more formal analysis, that the proper value for the coefficient in Eq. (5), from the criterion that E be a minimum for the nearly-free-electron gas, is $\gamma = 1$. This difference may appear rather large inasmuch as the first value also stems from the variational principle (but with the approximation applied at a different stage). The exchange operator of the Hartree-Fock equation derives therefrom, and Löwdin⁴ has demonstrated that Eq. (4) gives the function that most closely approximates this operator.

However, it is not necessarily true that the function which most nearly reproduces the effect of the exchange operator cannot be replaced by one imparting a lower value to E . When the electrons are nearly free, $A(\mathbf{r})$ is nearly constant. Now consider an expansion of $A(\mathbf{r})$ in which the first, or dominant, term is constant. This term is important in relating $A(\mathbf{r})$ to the exchange operator, but it has an effect only upon ϵ_n , not upon ψ_n and, therefore, E . Hence, it is not unreasonable that one could lower E by applying some constant factor to the succeeding terms, which is, in essence, what one does in choosing a different value for γ .

Kohn and Sham's argument is justified for a slowly varying $w(\mathbf{r})$. If $w(\mathbf{r})$ varies sinusoidally, this restriction may be stated as requiring its wavelength to greatly exceed that of an electron possessing the Fermi energy. However, for the conduction electrons of a metal the periodicity of the crystal potential is of the order of that of an electron at the Fermi level. For this reason it was deemed proper to investigate the manner in which the optimum value of γ varies with the wavelength of $w(\mathbf{r})$, a relationship which can then be used in a higher-order approximation of the exchange potential that allows for the mixture of wavelengths occurring in an arbitrary $w(\mathbf{r})$.

Considering γ as a parameter and substituting $A_0(\mathbf{r})$ for $A(\mathbf{r})$ in Eq. (1), one may determine a γ -dependent E from the solutions. The condition for this E to be an extremum is

$$\gamma = (dW/d\gamma)/(dW_0/d\gamma), \quad (6)$$

² R. Gaspar, Acta Phys. Acad. Sci. Hung. 3, 263 (1954).

³ W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

⁴ P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

where W is the exchange energy,

$$W = q \iint d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1) r_{12}^{-1},$$

and W_0 is the corresponding free-electron approximation,

$$W_0 = \frac{3}{2} (6/\pi)^{1/3} q \int d\mathbf{r} \rho^{4/3}(\mathbf{r}).$$

For a system of free electrons, i.e., for $w=0$, the ratio on the right in Eq. (6) becomes indeterminate inasmuch as $\rho(\mathbf{r}_1, \mathbf{r}_2)$ becomes independent of γ . Hence, γ is resolved by treating w as a perturbation.

Accordingly, let the $2N$ electrons be confined to a cube of volume L^3 , giving for the unperturbed wave function

$$\psi_n^{(0)}(\mathbf{r}) = L^{-3/2} e^{i\mathbf{k}\cdot\mathbf{r}},$$

where (in the ground state)

$$k_n \leq k_N \rightarrow (6\pi^2 N)^{1/3} / L \text{ as } N \rightarrow \infty.$$

Applying perturbation theory with respect to

$$w(\mathbf{r}) = \sum_{\mathbf{k}} \sigma(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}},$$

where $\sigma^*(\mathbf{k}) = \sigma(-\mathbf{k})$, one obtains to the second order

$$q^{-1}W = 3(6/\pi)^{1/3} N^{4/3} L^{-1} + 2L^{-3} \sum_{\mathbf{k}} |\sigma(\mathbf{k})|^2 \mu^2(\gamma, \mathbf{k}) \beta^2(\mathbf{k}) G(\mathbf{k}) \quad (7)$$

and

$$q^{-1}W_0 = 3(6/\pi)^{1/3} N^{4/3} L^{-1} [1 + 2(L^3/3N)^2 \times \sum_{\mathbf{k}} |\sigma(\mathbf{k})|^2 \mu^2(\gamma, \mathbf{k}) \beta^2(\mathbf{k})],$$

where, with

$$p_n^{-1}(\mathbf{k}) = \mathbf{k} \cdot (2\mathbf{k}_n + \mathbf{k}),$$

are defined

$$\beta(\mathbf{k}) = L^{-3} \sum_{n=1}^N [p_n(\mathbf{k}) + p_n(-\mathbf{k})],$$

$$\mu^{-1}(\gamma, \mathbf{k}) = 1 + q \left[2 \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} r_{\mathbf{r}}^{-1} - \frac{1}{3} (6/\pi)^{1/3} \gamma N^{-2/3} L^2 \right] \beta(\mathbf{k}),$$

and

$$\beta^2(\mathbf{k}) G(\mathbf{k}) = \sum_{n=1}^N \sum_{m=1}^N \int d\mathbf{r} e^{i(\mathbf{k}_n - \mathbf{k}_m) \cdot \mathbf{r}} r_{\mathbf{r}}^{-1} \times [p_n^2(\mathbf{k})(e^{i\mathbf{k}\cdot\mathbf{r}} - 1) + p_n(\mathbf{k}) p_m(\mathbf{k}) + p_n(\mathbf{k}) p_m(-\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}].$$

Assuming N is sufficiently large to permit the substitution of integrations for the above summations over n and m , one finds

$$8\pi^2 k_N^{-1} \beta(\mathbf{k}) = 1 + \frac{1}{4} \eta^{-1} (1 - \eta^2) \ln \zeta,$$

where $\eta = k/2k_N$ and $\zeta = (1+\eta)^2/(1-\eta)^2$, and

$$G(\mathbf{k}) = \pi L^6 k_N^{-2} g(\eta),$$

where

$$\begin{aligned} & 2\eta \left(1 + \frac{1-\eta^2}{4\eta} \ln \zeta \right)^2 g(\eta) \\ &= \left(1 + \frac{1-\eta^2}{4\eta} \ln \zeta \right) \int_1^\zeta \frac{dx}{x} \left(\frac{x+1}{x-1} \right) \ln x \\ & \quad - \frac{(1-\eta^2)}{4\eta} \int_1^\zeta \frac{dx}{x} \left(\frac{x+1}{x-1} \right) \ln^2 x - \frac{(1+\eta^2)}{4\eta} \ln^2 \zeta. \end{aligned}$$

Applying these relations to Eq. (6), one sees that when $\sigma(\mathbf{k})$ vanishes except for a particular value of k

$$\gamma = g(\eta).$$

Table I depicts the function $g(\eta)$, for which $g(0) = 1$ (in agreement with Kohn and Sham's result), $g(1) = \frac{1}{6}\pi^2$, and $\lim_{\eta \rightarrow \infty} \eta^2 g(\eta) = \frac{1}{3}$.

When $\sigma(\mathbf{k})$ is not so restricted, the optimum value of γ is a weighted mean of $g(\eta)$. In this event it may be advantageous to apply a relation suggested by the paper of Hohenberg and Kohn⁵ whereby, after considering

$$\rho(\mathbf{r}) = \rho_0 + \rho_1(\mathbf{r}),$$

where $\rho_0 = L^{-3} \int d\mathbf{r} \rho(\mathbf{r})$, one expands in ρ_1 the exchange contribution to the functional representing the total energy of the system in accordance with

$$\begin{aligned} W &= 3(6/\pi)^{1/3} q \rho_0^{4/3} L^3 \\ & \quad + \int \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_1(\mathbf{r}_1) \rho_1(\mathbf{r}_2) K(r_{12}) + \dots \quad (8) \end{aligned}$$

Then, requiring ρ_1 to minimize this functional yields, to the same order of approximation as that of the previous discussion, the exchange potential

$$A_1'(\mathbf{r}_1) = \int d\mathbf{r}_2 \rho_1(\mathbf{r}_2) K(r_{12}),$$

or, differing by a constant,

$$A_1(\mathbf{r}_1) = \int d\mathbf{r}_2 \rho(\mathbf{r}_2) K(r_{12}). \quad (9)$$

The equivalence of Eqs. (7) and (8), irrespective of the $\sigma(\mathbf{k})$, can be shown to require

$$\pi r K(r) = 4q \int_0^\infty d\eta \eta g(\eta) \sin s\eta, \quad (10)$$

where $s = 2k_N r$.

⁵ P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

TABLE I. The function $g(\eta)$ and its approximation $g_0(\eta)$.

| η | $g(\eta)$ | $g_0(\eta)$ | $g(\eta^{-1})$ | $g_0(\eta^{-1})$ |
|--------|-----------|-------------|----------------|------------------|
| 0.0 | 1.0000 | 1.000 | ... | ... |
| 0.1 | 1.0056 | 0.996 | 0.003351 | 0.003322 |
| 0.2 | 1.0228 | 0.993 | 0.01362 | 0.01316 |
| 0.3 | 1.0528 | 1.009 | 0.03149 | 0.02913 |
| 0.4 | 1.0981 | 1.059 | 0.05831 | 0.0506 |
| 0.5 | 1.1627 | 1.152 | 0.09638 | 0.0769 |
| 0.6 | 1.2536 | 1.283 | 0.1498 | 0.1071 |
| 0.7 | 1.3823 | 1.443 | 0.2266 | 0.1404 |
| 0.8 | 1.5698 | 1.616 | 0.3443 | 0.1758 |
| 0.9 | 1.8504 | 1.787 | 0.5570 | 0.2126 |
| 1.0 | 1.6449 | 1.934 | 1.6449 | 1.934 |

Equations (2) and (9) imply that $\frac{1}{2}K(r)$ serves the exchange potential as does q/r the Coulomb potential. From the asymptotic behavior of $g(\eta)$ it follows that

$$\lim_{r \rightarrow 0} rK(r) = \frac{2}{3}q,$$

i.e., the "exchange hole" associated with $A_1(\mathbf{r})$, roughly represented by $e\rho_0 rK(r)/q$, has two-thirds the depth of that associated with $A(\mathbf{r})$. Moreover, the volume integral of $e\rho_0 rK(r)/q$ is considerably less than e .

Substituting the approximation,

$$\begin{aligned} g_0(\eta) &= (1+3\eta^2)^{-1} + a\eta^2 + b\eta^4 \quad \text{for } \eta < \eta_0 \\ &= (1+3\eta^2)^{-1} \quad \text{for } \eta > \eta_0, \end{aligned}$$

for $g(\eta)$ in Eq. (10) leads to the replacement of $K(r)$ by $K_0(r)$, denoted by

$$\begin{aligned} q^{-1} r K_0(r) &= \frac{2}{3} \exp(-s/\sqrt{3}) \\ & \quad + 4\pi^{-1} s^{-6} \{ [3a^2(\eta_0^2 s^2 - 2) + 5b(\eta_0^4 s^4 \\ & \quad - 12\eta_0^2 s^2 + 24)] \sin \eta_0 s - \eta_0 s [a s^2(\eta_0^2 s^2 - 6) \\ & \quad + b(\eta_0^4 s^4 - 20\eta_0^2 s^2 + 120)] \cos \eta_0 s \}. \end{aligned}$$

Setting $a = 2.535$, $b = -0.851$, and $\eta_0 = 1.1$ renders

$$\int_0^\infty dr r K_0(r) = \int_0^\infty dr r K(r)$$

and gives the similarity between $g_0(\eta)$ and $g(\eta)$ presented in Table I.

As regards the use of Eq. (5) in connection with the conduction electrons in metals, a universal choice for γ seems inappropriate. The value of η , determined from the fundamental component of the crystal potential, depends on the valence and, somewhat, on the type of lattice. Thus, for the alkali metals one has $\eta \approx 1.14$; for aluminum, $\eta \approx 0.77$. The corresponding $g(\eta)$ vary considerably. Taking the harmonics of the crystal potential into account would be expected to lower the optimum value for γ .