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Perturbation Theory Using a Reduced Set of States

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A method is given whereby a second-order calculation of the energy due to a perturbation H_{en} of the zero-order Hamiltonian $H_e+H_p+H_{ep}$ can be evaluated approximately using only the eigenstates ψ_e and relaxation times τ_{ep}. As an example the Ruderman-Kittel formula for the exchange-type coupling of nuclear spins is re-evaluated.

I. INTRODUCTION

THERE are a number of examples in the literature[1–3] of perturbation theory being employed using eigenfunctions arising from only part of the unperturbed Hamiltonian. It is the purpose of this note to investigate the error involved in this procedure.

To have an example in mind, we examine the model of exchange-type coupling of nuclear spins in a metal.[1] The interaction can be thought of as arising from an electron scattering from one nucleus followed by a scattering from the second nucleus. In the previous calculation[1] account was not taken of the possibility of phonon scattering. With this in mind, it is clear that for distances where there is a finite chance of phonon scattering the interaction given in reference 1 is modified.

II. GENERAL FORMULATION

We repeat the calculation using as our basic states the eigenfunctions of the total Hamiltonian which can be schematically written as

$$H=H_{\text{electron}}+H_{\text{phonon}}+H_{\text{electron, phonon}}. \qquad (1)$$

The perturbation is the Fermi contact hyperfine interaction[4]

$$H_{\text{electron, nucleus}}=\sum_j \sum_i (8\pi/3) I_j\cdot S_i \delta(r_j) \qquad (2)$$

of the conduction electrons with the nuclear spins. Including a temperature average over the initial states the second-order correction to the energy is given as

$$\Delta E_2=\frac{1}{\mathrm{Tr}e^{-H/kT}}\sum{}'_{nm}\, e^{-E_m/kT}\langle m/H_{en}/n\rangle\langle n/H_{en}/m\rangle/(E_m-E_n), \qquad (3)$$

where the prime indicates $m\neq n$. Equation (3) can be rewritten as

$$\Delta E_2=\frac{1/2\lim\limits_{\epsilon\to 0}}{\mathrm{Tr}e^{-H/kT}}\sum_{m,n} e^{-E_m/kT}\langle m/H_{en}/n\rangle\langle n/H_{en}/m\rangle \times[1/(E_m-E_n-i\epsilon)+1/(E_m-E_n+i\epsilon)]. \qquad (4)$$

Using the alternative forms

$$\frac{1}{x-i\epsilon}=i\int_0^\infty e^{ixt-\epsilon t}dt, \qquad (5)$$

$$\frac{1}{x+i\epsilon}=-i\int_0^\infty e^{-ixt-\epsilon t}dt. \qquad (6)$$

Equation (4) can be further rewritten as

$$\Delta E_2=\frac{i/2}{\mathrm{Tr}e^{-H/kT}}\int_{0,\ \epsilon\to 0}^{\infty}\mathrm{Tr}\{e^{-H/kT}e^{iHt/\hbar}H_{en}e^{-iHt/\hbar}H_{en}e^{-\epsilon t} - e^{-H/kT}e^{-iHt/\hbar}H_{en}e^{iHt/\hbar}H_{en}e^{-\epsilon t}\}dt. \qquad (7)$$

Now in the standard way we can write[5]

$$e^{i(H_e+H_p+H_{ep})t/\hbar}=e^{iH_et/\hbar}e^{iH_pt/\hbar}G(e,p,t), \qquad (8)$$

where

$$G(e,p,t)=1+i\int_0^t e^{-iH_et'/\hbar}e^{-iH_pt'/\hbar}\times H_{ep}e^{iH_et'/\hbar}e^{iH_pt'/\hbar}G(e,p,t')dt', \qquad (9)$$

and

$$e^{-i(H_e+H_{ep}+H_p)t/\hbar}=F(e,p,t)e^{-iH_et/\hbar}e^{-iH_pt/\hbar}, \qquad (10)$$

where

$$F(e,p,t)=1-i\int_0^t e^{iH_et'/\hbar}e^{iH_pt'/\hbar}\times H_{ep}e^{-iH_et'/\hbar}e^{-iH_pt'/\hbar}F(e,p,t')dt'. \qquad (11)$$

Substituting Eqs. (8)–(11) into Eq. (7) one has

$$\Delta E_2=\frac{(i/2)}{\mathrm{Tr}e^{-H/kT}}\int_{0,\ \epsilon\to 0}^{\infty}\mathrm{Tr}\{e^{-H/kT}e^{iH_et/\hbar}e^{iH_pt/\hbar}G(e,p,t)\times H_{en}F(e,p,t)e^{-iH_et/\hbar}e^{-iH_pt/\hbar}H_{en}e^{-\epsilon t} - e^{-H/kT}F(e,p,t)e^{-iH_et/\hbar}e^{-iH_pt/\hbar}\times H_{en}e^{iH_et/\hbar}e^{iH_pt/\hbar}G(e,p,t)H_{en}e^{-\epsilon t}\}dt. \qquad (12)$$

Before taking the trace over the phonon coordinates an approximation is made by writing

$$e^{-H/kT}=e^{-H_e/kT}e^{-H_p/kT}G(e,p,-i/kT)\approx e^{-H_e/kT}e^{-H_p/kT}.$$

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[1] M. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[2] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1690 (1955).
[3] H. Suhl, Phys. Rev. **109**, 606 (1958).
[4] V. Weisskopf, Ann. Physik **9**, 23 (1931).
[5] R. Karplus, Phys. Rev. **73**, 1027 (1948).

The effect of this approximation is to slightly miscalculate ΔE_2, but for our purposes this effect is unimportant for it is the same for any two nuclei irrespective of their distance apart. Next, the trace is taken over the phonon coordinates simplifying Eq. (12) to

$$\Delta E_2=\frac{(i/2)}{\mathrm{Tr}e^{-H/kT}}\int_{0}^{\infty}\mathrm{Tr}_e\sum_{p,p'}\{e^{-H_e/kT}e^{-E_p/kT}e^{iH_et/\hbar}\times\langle p/G(ept)/p'\rangle H_{en}\langle p'/F(ept)/p\rangle e^{-iH_et/\hbar}H_{en}e^{-\epsilon t}-e^{-H_e/kT}e^{-E_p/kT}\langle p/F(ept)/p'\rangle e^{-iH_et/\hbar}\times\langle p'/G(ept)/p\rangle H_{en}e^{-\epsilon t}\}dt. \quad (13)$$
$(\epsilon\to 0)$

The most general matrix element of Eq. (13) in the electron representation includes three different sets of intermediate electron states. We only sum over those intermediate states for which G and F are to be considered diagonal in the electron representation. For those familiar with the Wangness-Bloch[6] derivation of the spin-density matrix equation this is equivalent to keeping the diagonal relaxation terms and neglecting the off diagonal as being shorter. The result is that

$$E_2=\frac{(i/2)}{\mathrm{Tr}e^{-H/kT}}\Big\{\int_0^\infty \sum_{e,e'}e^{-E_e/kT}e^{i(E_e-E_{e'})t/\hbar}e^{-\epsilon t}\langle e/H_{en}/e'\rangle\times\langle e'/H_{en}/e\rangle\sum_{p,p'}\langle ep/G/p'e\rangle\langle e'p'/F/pe'\rangle e^{-E_p/kT}-\int_0^\infty\sum_{e,e'}e^{-E_e/kT}e^{-i(E_e-E_{e'})t/\hbar}e^{-\epsilon t}\langle e/H_{en}/e'\rangle\times\langle e'/H_{en}/e\rangle\sum_{p,p'}\langle ep/F/p'e\rangle\times\langle e'p'/G/pe'\rangle e^{-E_p/kT}\Big\}dt. \quad (14)$$

As is shown in the Appendix we can approximately set

$$\sum_{pp'}(e^{-E_p/kT}/\mathrm{Tr}e^{-H_p/kT})\langle ep/G/p'e\rangle\times\langle e'p'/F/pe'\rangle\approx e^{-t/\tau}, \quad (15)$$

which simplifies Eq. (14) as

$$E_2=\frac{-(i/2)}{\mathrm{Tr}e^{-H_e/kT}}\sum_{e,e'}\left[\frac{\langle e/H_{en}/e'\rangle\langle e'/H_{en}/e\rangle e^{-E_e/kT}}{i(E_e-E_{e'})\hbar-1/\tau}-\frac{\langle e/H_{en}/e'\rangle\langle e'/H_{en}/e\rangle e^{-E_e/kT}}{-i(E_e-E_{e'})/\hbar-1/\tau}\right], \quad (16)$$

where $e^{-\epsilon t}$ has been dropped as τ assures the vanishing of the integral at the upper limit. Equation (16) is, of course, just the form one might have "guessed" to have been correct.[7]

[6] R. K. Wangness and F. Bloch, Phys. Rev. **89**, 728 (1953).
[7] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930).

III. APPLICATION TO RUDERMAN-KITTEL FORMULA

The Ruderman-Kittel formula[1] is now corrected assuming Eq. (16) is the correct form of second-order perturbation theory. They showed that their formula can be written as proportional to

$$\int_{-k_m}^{k_m}ke^{ikR}dk[\mathrm{P.P.}]\left[\int_{-\infty}^{\infty}\frac{k'e^{ik'r}dk'}{k'^2-k^2}-\int_{-k_m}^{k_m}\frac{k'e^{ik'R}dk'}{k'^2-k^2}\right], \quad (17)$$

where k_m is the Fermi momentum, R is the distance between nuclear sites, and P.P. means principal part. Including the effects of scattering, we can rewrite this as

$$\mathrm{Re}\int_{-k_m}^{k_m}ke^{ikR}\left[\int_{-\infty}^{\infty}\frac{k'e^{ik'R}dk'}{k'^2-k^2-i\delta^2}-\int_{-k_m}^{k_m}\frac{k'e^{ik'R}dk'}{k'^2-k^2-i\delta^2}\right]dk, \quad (18)$$

where $\delta^2=2m/h\tau$ and Re mean real part.

The first integral in the brackets can be integrated by the method of residues and the second integral can be shown to be zero. The result is that Eq. (18) becomes

$$-2\pi k_m^2\int_0^1 v\sin(vk_mR)\times\exp\left\{\frac{-Rk_m}{\sqrt{2}}[(\delta^4/k_m^4+v^4)^{1/2}-v^2]^{1/2}\right\}\times\cos\left\{\frac{k_m}{\sqrt{2}}R[(\delta^4/k_m^4+v^4)^{1/2}+v^2]^{1/2}\right\}dv. \quad (19)$$

Some numerical evaluations of Eq. (19) are given in Fig. 1. It is clear from the form of Eq. (19) that for a nonzero δ and large R the interaction is much weaker than for $\delta=0$—this is just another way of saying that for large R the electron most certainly has scattered before it has reached the second nucleus.

IV. CONCLUSION

It has been shown that one can take partial account of the missing states when doing perturbation theory with a partial set of states. The method has been applied in detail to the exchange-type coupling of nuclear spins in a metal[1] where the effect is expected to be the most apparent.

Suhl[3] has calculated, by second-order perturbation theory, the exchange-type coupling of nuclear spins in a ferromagnet. His result modified to include scattering

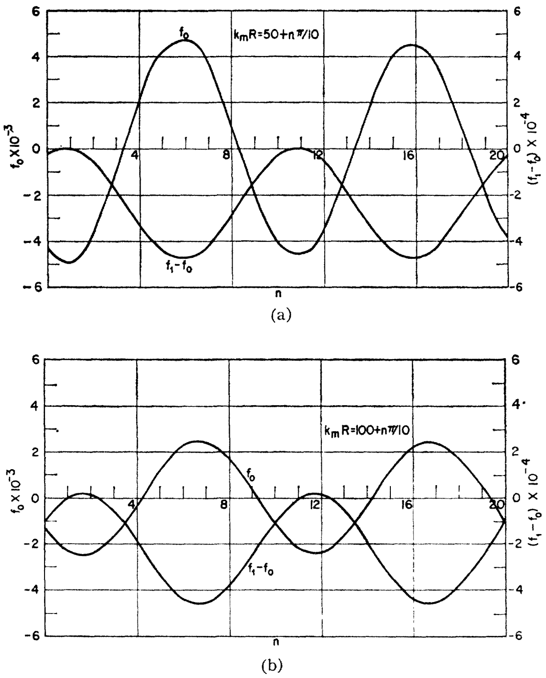

FIG. 1.

$$f_0=[(\text{Eq. }19)/-2\pi k_m^2]_{\beta=0}$$

and

$$f_1=[(\text{Eq. }19)/-2k_m^2]_{\beta=0.002},$$

where $\beta=\delta^2/k_m^2$. The value of β is approximately correct for Li at room temperature. Right-hand scale should read 10^{-2}.

is

$$H_{\text{eff}}=\frac{-A^2S}{8g\mu_\beta H_{\text{ex}}}\sum_{i\neq j}\frac{a}{R_{ij}}\exp\left\{-\frac{R_{ij}}{\sqrt{2}}[A+(A^2+B^2)^{1/2}]^{1/2}\right\}\times\cos\left\{\frac{R_{ij}}{\sqrt{2}}[-A+(A^2+B^2)^{1/2}]^{1/2}\right\}I_i^-I_j^+, \quad (20)$$

where

$$A=H_{\text{int}}/a^2H_{\text{ex}},\quad B=(g\mu_\beta H_{\text{ex}}a^2\tau)^{-1},$$

and the rest of the symbols are defined in reference 3. Suhl's original result is obtained by letting $B\rightarrow 0$.

In semiconductors[2] the added effect of scattering on the nuclear exchange-type coupling is small as the band gap already provides a large exponential damping.

APPENDIX

In Eq. (15) it is written that

$$\sum_{p,p'} e^{-E_p/kT}\langle ep/G/p'e\rangle\langle e'p'/F/pe\rangle/\mathrm{Tr}e^{-H_p/kT}\approx e^{-t/\tau}. \quad (A1)$$

To see this we must expand Eq. (9) as,

$$G(e,p,t)=1+i\int_0^t e^{-iH_et'/\hbar}e^{-iH_pt'/\hbar}H_{ep}e^{iH_et'/\hbar}e^{iH_pt'/\hbar}dt' - \int_0^t e^{-iH_et'/\hbar}H_{ep}e^{iH_et'/\hbar}e^{iH_pt'/\hbar}dt' \times\int_0^{t'} e^{-iH_et''/\hbar}e^{-iH_pt''/\hbar}H_{ep}e^{iH_et''/\hbar}e^{iH_pt''/\hbar}dt'' + \text{higher order terms,} \quad (A2)$$

and take Eq. (A2) between the states ep and ep', the result is that

$$\langle ep/G/ep'\rangle =\delta_{pp'}-\sum_{e'',p''}\int_0^t dt'\int_0^{t'}dt'' \times e^{-i(E_e-E_{e''}+E_p-E_{p''})(t'-t'')/\hbar}/\langle ep/H_{ep}/e''p''\rangle/^2\delta_{pp'} + \text{higher order terms.} \quad (A3)$$

Writing

$$(E_e-E_{e''}+E_p-E_{p''})=\Delta E, \quad (A4)$$

one has that

$$\int_0^t dt'\int_0^{t'}dt''e^{-i\Delta E(t'-t'')/\hbar} =\frac{1-\cos\Delta Et/\hbar}{(\Delta E)^2/\hbar^2}+i\frac{\sin\Delta Et/\hbar}{(\Delta E)^2/\hbar^2}-\frac{t}{\Delta E/\hbar}. \quad (A5)$$

Noting that $(1-\cos\Delta Et)/\hbar t(\Delta E)^2/\hbar^2$ behaves as a delta function with respect to integration over E and that the complex part of (A5) is odd with respect to E we see that Eq. (A1) becomes approximately

$$1-t/2\tau-t/2\tau\cdots\approx e^{-t/\tau}, \quad (A6)$$

where

$$1/\tau=2\pi\sum_{e''}\sum_{pp''}e^{-E_p/kT}|\langle ep/H_{ep}/e''p''\rangle|^2/\mathrm{Tr}e^{-E_p/kT}. \quad (A7)$$