The formula for the half-life given by Bethe and corrected for the theoretically calculated conversion coefficients (Hebb and Nelson) gives the half-life $2\times10^{-1}$ sec. for $l=3$ and $3\times10^{5}$ sec. for $l=4$ (experimental value $6.5\times10^{3}$ sec.). According to the curves of Flügge,[6] $N_K/N_L\approx0.1$ for $l=4$ and $N_K/N_L\approx0.4$ for $l=3$ (electric radiation). The recently published curves of Tralli and Lowen[7] give $N_K/N_L\approx3$ for $l=3$ and magnetic radiation. For electric octupole radiation the agreement between the experimental value 0.44 of $N_K/N_L$ and the theoretical one is very good. The half-life and internal conversion coefficients, however, indicate a mixture of $\approx70$ percent electric $2^4$-pole and $\approx30$ percent magnetic $2^3$-pole radiation. This would then still be an example of a parity forbidden isomeric transition.[8]

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## The Effect of Electronic Paramagnetism on Nuclear Magnetic Resonance Frequencies in Metals

C. H. TOWNES*
*Columbia University, New York, New York*
CONYERS HERRING
*Bell Telephone Laboratories, Murray Hill, New Jersey*
AND
W. D. KNIGHT*
*Trinity College, Hartford, Connecticut*
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THE nuclear paramagnetic resonance frequency for an atom in the metallic state usually is appreciably greater than the resonance frequency when the atom is in a non-metallic compound.[1] These frequency shifts are of the order of a few tenths of one percent, and are hence much too large to be accounted for by a simple difference in magnetic susceptibility of the materials or by differences in diamagnetic correction for the metallic and non-metallic atoms. It is proposed that such shifts are primarily due to orientation by the magnetic field of the spins of conduction electrons near the top of the Fermi distribution, and the interaction of these electrons with the nuclei. Since the conduction electrons usually have a very large probability density near the nucleus, this may be understood as an enormous concentration of the local magnetic susceptibility of the metal in the vicinity of the nuclei. It may also be compared with and calculated from the magnetic hyperfine structure interactions in an isolated atom. Diamagnetic effects of the same type appear to be very much smaller since the electronic currents responsible for the diamagnetism of the conduction electrons are appreciable only in the outer regions of the atom.

The fractional shift in nuclear resonance frequency between metal and non-metal is simply the fractional amount by which the presence of the conduction electrons increases the mean magnetic field strength $H$ at the nucleus. Neglecting the small diamagnetic effect, we consider only the field $\Delta H$ due to the electron spins, which is $8\pi/3$ times the mean density of spin moment at the nucleus, assuming cubic symmetry. If the electron distribution is not cubically symmetric about the nucleus, then electron density at points other than at the nucleus contributes to $\Delta H$, and $\Delta H$ will depend to some extent on orientation of the crystal with respect to $H$. In terms of wave functions of individual electrons in the metal the spin moment density at the nucleus can be written $\chi_p MH\langle|\psi_F(0)|^2\rangle_{Av}$, where $\chi_p$ is the spin contribution to the macroscopic susceptibility per unit mass, $M$ is the mass of one atom, and $\langle|\psi_F(0)|^2\rangle_{Av}$ is the average probability density at the nucleus for all electronic states on the Fermi surface. Now the hyperfine structure splitting $\Delta\nu$ for an $s$ electron in the free atom is proportional to $|\psi_a(0)|^2$, where $\psi_a$ is the wave function of the $s$ electron in the free atom. Dividing the above expression for $\Delta H$ by the familiar Fermi expression for $\Delta\nu$ gives the fractional frequency shift in terms of a ratio of metallic and atomic wave functions:

$$\frac{\Delta H}{H}=\frac{hc\Delta\nu I\chi_p M}{\mu_I\mu_e(2I+1)}\,\frac{\langle|\psi_F(0)|^2\rangle_{Av}}{|\psi_a(0)|^2} \tag{1}$$

where $hc\Delta\nu$ is the hyperfine splitting in energy units, $\mu_e$ is the Bohr magnetron, $\mu_I$ is the nuclear moment, and $I$ the nuclear spin.

TABLE I. Observed shifts of nuclear resonances in metals due to free electron paramagnetism, and comparison with theory.

| Nucleus | H.f.s. splitting $\Delta\nu$, in cm$^{-1}$ for $s$ electron | Observed shift $\Delta H/H$, (percent) | $\chi_p$ per gram$\times10^6$ | $\chi_p\langle|\psi_F(0)|^2\rangle_{Av}/|\psi_a(0)|^2\times10^6$ theory | from (1) |
|---|---|---|---|---|---|
| $Li^7$ | 0.027 | 0.04 | 3.0[a] | ~2.3 | 2.6 |
| $Na^{23}$ | 0.060 | 0.10 | 0.98[b] | 0.80 | 0.63 |
| $Cu^{63}$ | 0.39 | 0.23 | ~0.11[c] | | 0.078 |
| $Be^9$ | 0.040 | <0.002 | ~0.30[d] | ~0.15 | <0.025[e] |
| $Pb^{207}$ | 2.1[f] | 1.2 | ~0.10[c] | | 0.0091 |
| $Al^{27}$ | 0.35[f] | 0.16 | ~0.47[c] | | 0.21 |
| $Ca^{69}$ | 0.58[f] | 0.44 | ~0.20[c] | | 0.083 |

[a] Measured value with diamagnetic corrections, S. R. Rao and K. Sarithri, Proc. Ind. Acad. **6**, 207 (1942).
[b] Average of measured values with diamagnetic corrections, F. Bitter, Phys. Rev. **36**, 978 (1930).
[c] Calculated value assuming free valence electrons.
[d] Theoretical value (reference 3).
[e] The small diamagnetic contribution to the shift may increase this limit by a factor of 2 or so.
[f] Estimated from Goudsmit's formula and measured values for ionized atoms.

We have attempted to calculate the theoretical value of the last factor in (1) for the cases (Na, Li, Be) for which adequate calculations of metallic wave functions are at present available. This factor may be written $(|\psi_0(0)|^2/|\psi_a(0)|^2)\bar{s}_K$, where $\psi_0$ is the wave function of an electron at the bottom of the conduction band and $\bar{s}_K$ is the mean over the Fermi surface of

$$s_k=(|\psi_k(0)|^2)/(|\psi_0(0)|^2).$$

Calculations by the Wigner-Seitz method[2] give $\psi_0$; $\bar{s}_k$ can be determined in either of two ways. The first, suitable only for monovalent metals, is to assume that $s_k$ is adequately represented by the first two terms of its development in powers of the square of the electronic wave vector $k$:

$$s_k=1+k^2ds_k/d(k^2)+\cdots, \tag{2}$$

and to use the expression given by Herring and Hill[3] for $ds_k/d(k^2)$ (Appendix III of this reference; a factor 6 should be inserted before $\alpha$ in Eq. (M).) This method was applied to the case of Na with the aid of wave functions kindly supplied by Dr. Bardeen, and gave $\bar{s}_k=0.70$. Similar calculations were made for Li, but no results will be quoted because it was found that the available wave functions were based on an incorrect potential field for the Li ion. Comparison with the case of Be, to be discussed next, suggests that $\bar{s}_k$ for Li may be of the order of 0.4. For Be, which is divalent, the first two terms of (2) do not give at all a good approximation, and a second procedure was therefore adopted. This consisted in dividing up the Fermi surface into six portions, estimating an average $s_k$ for each portion from the values of $s_k$ directly calculated for states near the Fermi surface (Table VII of reference 3), and combining with suitable weights. This gave $\bar{s}_k=0.32$, and this value did not seem to be particularly sensitive to changes in the technique of averaging.

The quantity $|\psi_0(0)|^2/|\psi_a(0)|^2$ has approximately the values 1.16, 1.9, and 1.6, for Na, Li, and Be, respectively. For other metals its behavior can be inferred qualitatively by noting how much of the charge of the outermost $s$ electrons of the free atom lies outside a sphere whose volume equals the atomic volume of the metal; it appears from this that $|\psi_0(0)|^2/|\psi_a(0)|^2$ should be appreciably smaller for such multivalent metals as Al, Ga, and Pb than for the mono- and divalent ones.

Table I gives some experimental values of the relative frequency shift, values of $\chi_p(|\psi_F(0)|^2)_{Av}/|\psi_a(0)|^2$ computed from these shifts by use of (1), and, for Li, Na, and Be, the results of theoretical attempts to calculate this product by the methods outlined above. In almost all cases the most uncertain factor is probably the value of $\chi_p$. Though no quantitative comparisons of theory and experiment can be made at present for other metals than these three, it will be noted that the figures in the table are consistent with reasonable values for $\chi_p$, $|\psi_0(0)|^2/|\psi_a(0)|^2$, and $\delta_k$. The case of Be is interesting in that the shift is too small to measure, indicating values of $\delta_k$ and/or $\chi_p$ still smaller than those calculated. The shift in Pb illustrates the considerable size which this paramagnetic effect may have in heavy metals.

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## Relativistic Nuclear Force

T. TOYODA
*St Paul's University, Tokyo, Japan*
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SINCE experiments on neutron-proton scattering were extended to very high voltages at Berkeley,[1] theoretical calculations[2-4] have been made to obtain the relativistic correction to nuclear forces. One of the most remarkable alterations of the nuclear force brought out by the calculations is that the $1/r^3$ singularity of the tensor force disappears in the relativistically corrected forms. This change eliminates the essential difficulty of the calculation of the deuteron ground state. However, it must be mentioned that none of these theoretical attacks has fully taken into account the retardation effect of the mesonic potential. The calculation developed in this paper starts with the explicit expression of the retarded potential and will examine additional non-negligible terms which have hitherto been overlooked. One of these terms corresponds to Breit's expression for the Møller force in the case of two electrons.

We shall take the pseudoscalar meson field with only pseudoscalar coupling, so that we have

$$(\Delta-\partial_t^2-\kappa^2)U=\varphi, \tag{1}$$

where the natural units $\hbar=c=1$ are used, and $\kappa$ is the rest mass of the meson field $U$. The source function $\varphi$ is given by the transition matrix elements of the first nucleon between two states $(E_1, u_1)\rightarrow(E_1', u_1')$, i.e.,

$$\varphi(\mathbf{r}_1, t)=fu_1'^*(\mathbf{r}_1)\rho_2^{(1)}Q^{(1)}u_1(\mathbf{r}_1)\exp(i(E_1'-E_1)t), \tag{2}$$

where $f$, $\rho_2^{(1)}$ and $Q^{(1)}$ are respectively the coupling constant, a Dirac matrix and an isotopic spin operator of the first particle, in the usual sense of these symbols. $u_1(\mathbf{r}_1)$ is the Dirac spinor wave function.

Now it is clear that (1) has the following special solution:

$$U(\mathbf{r}_2, t)=f\exp(i(E_1'-E_1)t)\cdot\int u_1'^*(\mathbf{r}_1)\{Q^{(1)}\rho_2^{(1)} \times\exp[-|\mathbf{r}_2-\mathbf{r}_1|(\kappa^2-(E_1'-E_1)^2)^{\frac{1}{2}}]/|\mathbf{r}_2-\mathbf{r}_1|\}u_1(\mathbf{r}_1)dv_1. \tag{3}$$

Since we are interested in the correction due to the retardation effect, we shall expand the exponential function in the above integrand in power series in $(E_1'-E_1)$:

$$\begin{aligned}\exp(-|\mathbf{r}_2-\mathbf{r}_1|(\kappa^2-(E_1'-E_1)^2)^{\frac{1}{2}})/|\mathbf{r}_2-\mathbf{r}_1| &=\exp(-|\mathbf{r}_2-\mathbf{r}_1|\kappa)/|\mathbf{r}_2-\mathbf{r}_1| \\ &\quad+\exp(-|\mathbf{r}_2-\mathbf{r}_1|\kappa)(E_1'-E_1)^2/2\kappa+\cdots \\ &\equiv W_0+W_1+\cdots.\end{aligned} \tag{4}$$

The first term, $W_0$, is the usual static Yukawa potential, and the second term, $W_1$, is the first correction term arising from the retardation.

The succeeding calculation can be performed in an analogous fashion to that of the Møller force between two electrons.[5] The transition matrix element $(E_1, u_1; E_2, u_2)\rightarrow(E_1', u_1'; E_2', u_2')$ is given as follows, provided the first nucleon is a proton and the second a neutron:

$$\begin{aligned}V&=\int U(\mathbf{r}_2t)\cdot\varphi(\mathbf{r}_2, t)dv_2 \\ &=-f^2\exp(i(E_1'+E_2'-E_1-E_2)t)\cdot\int\int u_2'^*(\mathbf{r}_2)\cdot u_1'^*(\mathbf{r}_1)\rho_2^{(2)}\rho_2^{(1)} \\ &\quad\times\{\exp(-|\mathbf{r}_2-\mathbf{r}_1|(\kappa^2-(E_1'-E_1)^2)^{\frac{1}{2}})/ \\ &\qquad|\mathbf{r}_2-\mathbf{r}_1|\}u_2(\mathbf{r}_2)u_1(\mathbf{r}_1)dv_1\cdot dv_2 \\ &=\int\int u_2'u_1'(-f^2\rho_2^{(2)}\rho_2^{(1)}W_0-f^2\rho_2^{(2)}\rho_2^{(1)}W_1-\cdots)u_2\cdot u_1dv_1\cdot dv_2.\end{aligned} \tag{5}$$

The operator expression in the parentheses in (5) is usually called the nuclear force between two particles, although the first and the second terms in the parentheses, as will be shown later, represent quantities of the same order. Attention has hitherto been limited to the discussion of the first term. The second term, in which we are particularly interested, can be re-written in a commutator form:

$$-f^2\rho_2^{(2)}\rho_2^{(1)}W_1=-f^2[H_2, \rho_2^{(2)}[H_1, \rho_2^{(1)}\exp(-|\mathbf{r}_2-\mathbf{r}_1|\kappa)]]/2\kappa \tag{6}$$

where $H_i$ is the Dirac Hamiltonian of a free nucleon, i.e.,

$$H_i=-i\boldsymbol{\alpha}_i\cdot\mathrm{grad}_i+\beta_i\mu \quad (i=1, 2). \tag{7}$$

Equation (6) can be written also as

$$\begin{aligned}&-f^2\rho_2^{(2)}\rho_2^{(1)}W_1 \\ &=f^2\kappa\rho_3^{(2)}\rho_3^{(1)}\left\{(\boldsymbol{\sigma}_2, \boldsymbol{\sigma}_1)+\frac{(\boldsymbol{\sigma}_2, \mathbf{r}_{12})(\boldsymbol{\sigma}_1, \mathbf{r}_{12})}{r_{12}^2}\right\}\frac{e^{-\kappa r_{12}}}{r_{12}} \\ &\quad+f^2\kappa\rho_3^{(2)}\rho_3^{(1)}\frac{(\boldsymbol{\sigma}_2, \mathbf{r}_{12})(\boldsymbol{\sigma}_1, \mathbf{r}_{12})}{r_{12}^2}\cdot\frac{e^{-\kappa r_{12}}}{1/\kappa} \\ &\quad+4f^2\mu^2\rho_1^{(2)}\rho_1^{(1)}e^{-\kappa r_{12}} \\ &\quad-2f^2\mu\kappa i\{\rho_1^{(2)}\rho_3^{(1)}(\boldsymbol{\sigma}_1, \mathbf{r}_{12})+\rho_3^{(2)}\rho_1^{(1)}(\boldsymbol{\sigma}_2, \mathbf{r}_{21})\}\frac{e^{-\kappa r_{12}}}{r_{12}} \\ &\quad+2f^2\kappa\rho_3^{(2)}\rho_3^{(1)}\frac{e^{-\kappa r_{12}}}{r_{12}}\{(\boldsymbol{\sigma}_1, \mathbf{r}_{12})\cdot(\boldsymbol{\sigma}_2, \mathrm{grad}_2)+(\boldsymbol{\sigma}_2, \mathbf{r}_{21})(\boldsymbol{\sigma}_1, \mathrm{grad}_1)\} \\ &\quad-4f^2\rho_3^{(2)}\rho_3^{(1)}e^{-\kappa r_{12}}(\boldsymbol{\sigma}_2, \mathrm{grad}_2)(\boldsymbol{\sigma}_1, \mathrm{grad}_1) \\ &\qquad+4f^2\mu ie^{-\kappa r_{12}}\{\rho_1^{(2)}\rho_3^{(1)}(\boldsymbol{\sigma}_1, \mathrm{grad}_1)+\rho_3^{(2)}\rho_1^{(1)}(\boldsymbol{\sigma}_2, \mathrm{grad}_2)\}.\end{aligned} \tag{8}$$

The first term in this last expression (8) is the counterpart of Breit's force for the case of nuclear interaction. The second term is worth particular attention since its effect decreases with $r$ less rapidly than the other terms. The effect of this term may, therefore, become predominant in the calculation of the quadrupole moment of the deuteron. The third and fourth terms, which contain $i\rho_1$, unfortunately cannot be reduced to simpler forms, even in Pauli's approximation. Indeed, $\rho_3$ is of the order of unity, while $i\rho_1$ is of the same order as $\rho_2$ in this approximation. Therefore, we cannot neglect these terms.

On the other hand, the last three terms in (8) are non-diagonal in the $\mathbf{r}$ representation, and express the dependence on the relative velocity of the two nucleons. When the de Broglie wave-length of an incident neutron approaches the force range $1/\kappa$, these non-diagonal parts will become of the same order as the other terms.

If we take a scalar instead of a pseudoscalar interaction, the retardation effect gives only corrections of higher order. The pseudoscalar type of interaction resembles that of the vector type in the sense that they both contain the effect of the nucleonic current. The detailed estimation of the above mentioned additional terms will be discussed in a full report.

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