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ABSTRACT

A review of the theory of Zeeman effect is presented with specific attention to relativistic and diamagnetic effects. The single-electron problem is solved completely by reduction of the Dirac equation. This leads to the Breit-Margenau correction, which is proportional to the kinetic energy of the electron. The many-electron problem is treated approximately from the Breit-Dirac equation with a method based on Abragam and Van Vleck's investigation of atomic oxygen. The electron-electron interactions give rise to a correction to the classical Zeeman energy, which essentially depends on the electron density and can be interpreted as a diamagnetic effect. Formulas are developed for the matrix elements in the single-electron scheme, and a general expression is given for the total g-value correction in the case of equivalent electrons and Hund's-rule ground state. A new two-parameter radial wave function for the 4f electron is introduced, which can be fitted well to calculated Hartree functions. This wave function has been used to calculate the corrections to the g value for thulium, and the result is in excellent agreement with the experimental value.

RELATIVISTIC AND DIAMAGNETIC CORRECTIONS OF ATOMIC g VALUES[*]

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INTRODUCTION

The classical expression for the Zeeman effect is $Z = \mu_B \bar{B} \cdot (\bar{L} + 2\bar{S})$, where μ_B is the Bohr magneton, $\bar{B}$ the magnetic field, and $\bar{L}$ and $\bar{S}$ the total orbital and spin angular momenta in units of $\hbar$. The atomic g value (g_J) is defined by $Z = \mu_B g_J \bar{B} \cdot \bar{J}$, where $\bar{J} = \bar{L} + \bar{S}$, and, in the case of Russell-Saunders (RS) coupling, this gives rise to the usual Landé formula.

Accurate measurements of g values, however, particularly by the method of atomic beams, reveal that this simple description is insufficient. The Zeeman operator has now to be defined as the linear part of the total Hamiltonian, and the deviations between the experimental g values and the Landé values have mainly three sources, (a) partial breakdown of the RS coupling due to the spin-orbit coupling, (b) the anomalous magnetic moment of the electron (Schwinger correction), and (c) relativistic and diamagnetic effects.

We are here concerned only with the last part, and shall start with the single-electron case and use the standard technique of reducing the Dirac equation into one for the large components only.[1]

Single-Electron Case

The Dirac equation for an electron (with charge -e) in an electro-magnetic field $(\overline{A}, \phi)$ is

$$E\psi = [-c\,\overline{\alpha} \cdot (\overline{p} + e\overline{A}) - \beta\, mc^2 - e\phi]\,\psi,\qquad (1)$$

where $\alpha = \begin{pmatrix} 0 & \overline{\sigma} \\ \overline{\sigma} & 0 \end{pmatrix}$, $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, and E and $\overline{p}$ are the energy and momentum operators, respectively. The components of $\overline{\sigma}$ are the usual Pauli spin matrices, and 1 in the beta matrix stands for $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. (Note that we write $e\overline{A}$ instead of the more commonly used $\frac{e}{c}\,\overline{A}$, because we assume that all quantities are expressed in the same unit system.) Writing ψ_1 for the first two components and ψ_2 for the last two, we can separate Eq. (1) into

$$(E - V + mc^2)\,\psi_1 + c\,\overline{\sigma} \cdot (\overline{p} + e\overline{A})\,\psi_2 = 0,\qquad (2)$$

$$(E - V - mc^2)\,\psi_2 + c\,\overline{\sigma} \cdot (\overline{p} + e\overline{A})\,\psi_1 = 0,$$

where $V = -e\,\phi$. The first of these equations shows that, for a velocity of the electron $v \ll c$, ψ_1 is of the order of $(v/c)\,\psi_2$. If we eliminate ψ_1 and neglect terms of higher order than v^2/c^2, we get

$$(E' - V)\,\psi_2 = \frac{1}{2m}\,\overline{\sigma} \cdot (\overline{p} + e\overline{A})\,(1 - \frac{E' - V}{2mc^2})\,\overline{\sigma} \cdot (\overline{p} + e\overline{A})\,\psi_2,$$

$$(3)$$

where $E' = E - mc^2$. But we have

$$\overline{\sigma} \cdot (\overline{p} + e\overline{A})\,(E' - V) = (E' - V)\,\overline{\sigma} \cdot (\overline{p} + e\overline{A}) + i\hbar\,\overline{\sigma} \cdot \nabla V,$$

and Eq. (3) can be written

$$(E' - V)\psi_2 = \left\{ \frac{1}{2m} [\overline{\sigma} \cdot (\overline{p} + e\overline{A}]^2 - \frac{1}{4m^2c^2} (E' - V)[\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^2 \right.$$

$$\left. - \frac{i\hbar}{4m^2c^2} (\overline{\sigma} \cdot \nabla V) \overline{\sigma} \cdot (\overline{p} + e\overline{A}) \right\} \psi_2 .$$

Since $\dfrac{E' - V}{mc^2}$ is of the order of v^2/c^2, we can replace $(E' - V)$ on the right-hand side by $\dfrac{1}{2m} [\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^2$ and get

$$(E' - V)\psi_2 = \left\{ \frac{1}{2m} [\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^2 - \frac{1}{8m^3c^2} [\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^4 \right.$$

$$\left. - \frac{i\hbar}{4m^2c^2} (\overline{\sigma} \cdot \nabla V) \overline{\sigma} \cdot (\overline{p} + e\overline{A}) \right\} \psi_2 .$$

Now, the relation

$$(\overline{\sigma} \cdot \overline{a})(\overline{\sigma} \cdot \overline{b}) = \overline{a} \cdot \overline{b} + i\overline{\sigma} \cdot (\overline{a}x\overline{b}),$$

where $\overline{a}$ and $\overline{b}$ commute with $\overline{\sigma}$ but are elsewhere arbitrary, gives

$$[\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^2 = \overline{p}^2 + e(\overline{p} \cdot \overline{A} + \overline{A} \cdot \overline{p}) + e^2\overline{A}^2 + ie\overline{\sigma} \cdot (\overline{p}x\overline{A} + \overline{A}x\overline{p}).$$

But $\overline{p}x\overline{A} + \overline{A}x\overline{p} = -i\hbar\nabla x \overline{A} = -i\hbar\overline{B}$ and, if the magentic field is uniform, $\overline{A} = 1/2 \overline{B} x \overline{r}$ and $\overline{p} \cdot \overline{A} + \overline{A} \cdot \overline{p} = \hbar\overline{B} \cdot \mathcal{l}$, where $\mathcal{l} = \dfrac{1}{\hbar} \overline{r} x \overline{p}$. Then

$$\frac{1}{2m} [\overline{\sigma} \cdot (\overline{p} + e\overline{A})]^2 = \frac{\overline{p}^2}{2m} + \mu_B \overline{B} \cdot (\mathcal{l} + \overline{\sigma}) + \frac{e^2\overline{A}^2}{2m} ,$$

and similarly, since $\bar{p}$ commutes with $\bar{l}$ and $\bar{\sigma}$,

$$\frac{1}{4m^2}[\bar{\sigma}\cdot(\bar{p}+e\bar{A})]^4 = \frac{\bar{p}^4}{4m^2} + \mu_B\,\bar{B}\cdot(\bar{l}+\bar{\sigma})\frac{\bar{p}^2}{m}\,,$$

where we have left out terms of second and higher order in the magnetic field. We also get

$$(\bar{\sigma}\cdot\nabla V)\,\bar{\sigma}\cdot(\bar{p}+e\bar{A}) = \nabla V\cdot(\bar{p}+e\bar{A}) + i\bar{\sigma}\cdot[\nabla V\times(\bar{p}+e\bar{A})]\,,$$

and the complete Eq. (3) becomes

$$(E'-V)\psi_2 = \left\{\frac{\bar{p}^2}{2m} + \mu_B\,\bar{B}\cdot(\bar{l}+\bar{\sigma}) - \frac{\bar{p}^4}{8m^3c^2} - \mu_B\,\bar{B}\cdot(\bar{l}+\bar{\sigma})\frac{\bar{p}^2}{2m^2c^2}\right.$$

$$\left. -\frac{i\hbar}{4m^2c^2}\nabla V\cdot(\bar{p}+e\bar{A}) + \frac{\hbar}{4m^2c^2}\bar{\sigma}\cdot[\nabla V\times(\bar{p}+e\bar{A})]\right\}\psi_2\,.$$

$$(4)$$

The first two terms of Eq. (4) form the nonrelativistic Hamiltonian, the third term is the relativistic mass correction to the classical kinetic energy, and the fourth term the corresponding correction to the classical Zeeman energy. (Note that the latter correction is relatively twice as large as the former.) The fifth term has no simple classical interpretation and is difficult to observe experimentally. The term $\nabla V\cdot\bar{A}$ disappears if the magnetic field is uniform and V is spherically symmetric. The last term of Eq. (4) is the spin-orbit interaction, which, as is seen, also depends on the magnetic field.

In the following we assume that the magnetic field is uniform and that the potential V is spherically symmetric. We then have

$$\bar{\sigma}\cdot(\nabla V\times\bar{A}) = \frac{1}{2}\bar{\sigma}\cdot[\bar{r}\times(\bar{B}\times\bar{r})]\frac{1}{r}\frac{dV}{dr} = \frac{1}{2}\bar{B}\cdot\left(\bar{\sigma}-\frac{(\bar{\sigma}\cdot\bar{r})}{r^2}\bar{r}\right)r\frac{dV}{dr}\,,$$

and the total correction to the classical Hamiltonian becomes

$$\delta Z = -\mu_B \overline{B} \cdot (\overline{\ell} + \overline{\sigma}) \frac{T}{mc^2} + \frac{1}{4} \mu_B \overline{B} \cdot \left(\overline{\sigma} - \frac{(\overline{\sigma} \cdot \overline{r})}{r^2} \overline{r} \right) \frac{r \frac{dV}{dr}}{mc^2} \quad ,$$

(5)

where $T = \overline{p}^2/2m$ is the kinetic energy operator.

In spherical coordinates (r, θ, ϕ), with the polar axis (z axis) along the magnetic field, Eq. (5) can be written

$$\delta Z = -\mu_B B (\ell_z + \sigma_z) \frac{T}{mc^2} + \frac{1}{4} \mu_B B \left[\sigma_z \sin^2\theta - \frac{1}{2} \sin\theta \cos\theta (\sigma_+ e^{-i\phi} + \sigma_- e^{i\phi}) \right] \frac{r \frac{dV}{dr}}{mc^2} ,$$

where $\sigma_+ = \sigma_x + i\sigma_y = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}$ and $\sigma_- = \sigma_x - i\sigma_y = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}$. Using the

virial theorem, $\left\langle r \frac{dV}{dr} \right\rangle = 2 \left\langle T \right\rangle$, we get for the diagonal element

of δZ in a state characterized by the quantum numbers $(n\ell m_s m_\ell)$,

$$\left\langle n\ell m_s m_\ell \, | \, \delta Z \, | \, n\ell m_s m_\ell \right\rangle = -\mu_B B \left[m_\ell + 2m_s - m_s \left\langle \sin^2\theta \right\rangle \right] \frac{\left\langle T \right\rangle}{mc^2}$$

(6)

where $\left\langle \sin^2\theta \right\rangle = 2 \frac{\ell(\ell+1) - 1 + m_\ell^2}{(2\ell-1)(2\ell+3)}$.

The first two terms of Eq. (6) are the relativistic mass correction and the last term is the change in the spin-orbit coupling due to the magnetic field.

The off-diagonal elements of Eq. (5) can be obtained in the following way. We are interested only in elements between states of the same configuration, and we can therefore confine ourselves to single-electron elements diagonal in n and ℓ. With the notation of Condon and Shortley[2] we have

$$\left\langle n\ell\, m_s\, m_\ell \,\left|\, \tfrac{1}{2}\, \sin\theta\, \cos\theta\, \sigma_+ e^{-i\phi}\, \right|\, n\ell m_s{}'\, m_\ell{}' \right\rangle = \delta\,(m_\ell{}',\; m_\ell+1)\, \delta\,(m_s{}',\; m_s-1).$$

$$\int_0^\pi \Theta\,(\ell m_\ell)\, \Theta\,(\ell m_\ell{}')\, \sin\theta\, \cos\theta\, \sin\theta\, d\theta\,,$$

which shows that the operator is diagonal with respect to $m_j = m_s + m_\ell$.
Now $\sin\theta\, \cos\theta = -\sqrt{\tfrac{4}{15}}\; \Theta\,(2,1)$ and

$$\int_0^\pi \Theta(\ell m_\ell)\, \Theta(\ell' m_\ell{}')\, \Theta(k, m_\ell - m_\ell{}')\, \sin\theta\, d\theta = \sqrt{\frac{2k+1}{2}}\; c^k\,(\ell m_\ell,\; \ell' m_\ell{}')$$

gives

$$\left\langle n\ell\, m_s\, m_\ell \,\left|\, \tfrac{1}{2}\, \sin\theta\, \cos\theta\, \sigma_+ e^{-i\phi}\, \right|\, n\ell\, m_s-1\; m_\ell+1 \right\rangle = \sqrt{\tfrac{2}{3}}\; c^2(\ell m_\ell,\; \ell m_\ell+1)\,.$$

Therefore, the only nonvanishing off-diagonal elements of Eq. (5) become

$$\left\langle n\ell\, m_s\, m_\ell \,\left|\, \delta Z \,\right|\, n\ell\, m_{s+}-1\; m_\ell\pm1 \right\rangle = \mp\,\frac{1}{\sqrt{6}}\; \mu_B B\, c^2\,(\ell m_\ell,\; \ell m_\ell\pm1)\, \frac{\langle T\rangle}{mc^2}\,.$$

The coefficients c^2 are tabulated in Condon and Shortley (p. 179). Using
the formula given by Gaunt (Condon and Shortley p. 176) we get the
following general formula for the off-diagonal elements,

$$\left\langle n\ell\, m_s\, m_\ell \,\left|\, \delta Z \,\right|\, n\ell\, m_{s\;\mp}\, 1\, m_\ell\pm1 \right\rangle = \mu_B B\, \frac{2m_\ell\pm1}{2(2\ell-1)(2\ell+3)}\, [\ell(\ell+1)-m_\ell(m_\ell\pm1)]^{1/2}\, \frac{\langle T\rangle}{mc^2}\,.$$

$$(7)$$

With the vector-coupling coefficients and the formulas (6) and (7) one
can easily get the corresponding elements in the $(n\,\ell\,j\,m_j)$ scheme. The
diagonal elements become

$$\left\langle n\ell\, jm_j \,\middle|\, \delta Z \,\middle|\, n\ell\, jm_j \right\rangle = - \mu_B\, B\, m_j\, \frac{(j+1/2)^2}{j(j+1)} \cdot \frac{\langle T \rangle}{mc^2} \,. \qquad (8)$$

This formula is equivalent to the expressions given by Breit and Margenau,[3]
and this correction is therefore usually called the Breit-Margenau correction.
One can also derive this formula from Eq. (6), without calculating any off-
diagonal elements, by using the "diagonal-sum rule" and the fact that δZ
transforms as a vector, which means that the diagonal elements are
proportional to m_j .

In the following we use the formulas derived for the $(n\ell\, m_s m_\ell)$ scheme,
rather than the Breit-Margenau formula, since the former approach is more
convenient in applications to many-electron systems.

Many-Electron Case

The starting point in the many-electron problem is the extended Dirac
equation given by Breit,[4] which also includes electron-electron interactions.
The Zeeman Hamiltonian is obtained from this equation by the usual replace-
ment of $\bar{p}$ by $e\bar{A}$ and taking the linear part in $\bar{A}$. The correction to the
classical Zeeman operator is then given by

$$\delta Z = - \frac{\mu_B \bar{B}}{mc^2} \cdot \sum_i (\bar{\ell}_i + \bar{\sigma}_i)\, T_i - \frac{\mu_B\, e^2 Z}{8\pi\epsilon_0\, mc^2} \sum_i \bar{\sigma}_i \cdot \left(\nabla_i \frac{1}{r_i} \times \bar{A}_i \right) +$$

$$+ \frac{\mu_B e^2}{8\pi\epsilon_0\, mc^2} \sum_{\substack{i,k \\ k\neq i}} \sigma_i \cdot \left(\nabla_i \frac{1}{r_{ik}} \times \bar{A}_i \right) + \frac{\mu_B e^2}{4\pi\epsilon_0 mc^2} \sum_{\substack{i,k \\ k\neq i}} \bar{\sigma}_i \cdot \left(\nabla_k \frac{1}{r_{ik}} \times \bar{A}_k \right) -$$

$$- \frac{e^3}{8\pi\epsilon_0 m^2 c^2} \sum_{\substack{i,k \\ k\neq i}} \left[r_{ik}^{-1} (\bar{A}_k \cdot \bar{p}_i) + r_{ik}^{-3} (\bar{r}_{ik} \cdot \bar{A}_k)(\bar{r}_{ik} \cdot \bar{p}_i) \right] \,.$$

$$\qquad\qquad (9)$$

The first three terms of Eq. (9) correspond to the Breit-Margenau correction, discussed in the preceding section, and the last two terms can be interpreted as a diamagnetic correction. The former depend essentially on the kinetic energy of the valence electrons and the latter on the electron density in the core.

In order to calculate the matrix elements of Eq. (9) we shall, in principle, follow the approximate treatment given by Abragam and Van Vleck[5] in their discussion of the Zeeman effect in atomic oxygen. This operator involves two-electron operators of the type

$$G = \sum_{i,k}^{k \neq i} g(i,k),$$ where $g(i,k)$ operates on the coordinates of electron i and k. Therefore, antisymmetric wave functions give rise to integrals of exchange type (see Condon and Shortley p. 171). We shall, however, disregard this fact here and use as our basic functions simple products of single-electron wave functions (one term). The matrix elements in the general case are then obtained in a standard way if the wave functions are expressed as linear combinations of such terms.

We now show that the two-electron operator (9) is approximately equivalent to a single-electron operator. The diagonal element of G in a state A can be written

$$\langle A | G | A \rangle = \sum_{i,k}^{k \neq i} \iint \psi_i^*(\bar{r}) \psi_k^*(\bar{r}') g(\bar{r}\,\bar{r}') \psi_k(\bar{r}') \psi_i(\bar{r}) \, d\tau' \, d\tau =$$

$$= \sum_i \int \psi_i^*(\bar{r}) \left[\int \sum_k^{k \neq i} \psi_k^*(\bar{r}') g(\bar{r}\,\bar{r}') \psi_k(\bar{r}') \, d\tau' \right] \psi_i(\bar{r}) \, d\tau \, ,$$

where ψ_i is the single-electron wave function in the state i, and i and k run through all states of A. If $g(\bar{r}\,\bar{r}')$ is now an ordinary function of the coordinates, this expression is exactly the same as the diagonal element of the single-electron operator $F = \sum_i f(i)$, where

$$f(i) = \int \sum_k^{k \neq i} \psi_k^*(\bar{r}') g(\bar{r}_i \bar{r}') \psi_k(\bar{r}') \, d\tau' = \int \rho_i(\bar{r}') g(\bar{r}_i \bar{r}') \, d\tau' \, .$$

Here $\rho_i(\bar{r}') = \overset{k \neq i}{\underset{k}{\Sigma}} \; \psi_k^*(\bar{r}') \, \psi_k(\bar{r}')$ is the electron density from all

electrons except i. The summation over k must here be confined to the single-electron states appearing in the state F is operating on. In the following we assume that ρ_i is spherically symmetric, and then F becomes independent of the state it is operating on, as long as we confine ourselves to states within a given configuration (since equivalent electrons have identical radial parts).

In the same way one can also show that the off-diagonal elements between states that differ by one single-electron state are the same for F and G. Of course, in replacing G by F we drop elements between states that differ by two single-electron states. These elements, however, are much smaller than the elements of the other types, especially for heavy atoms, since the latter involve summations over all electrons.

These approximations might seem drastic at first sight, but it turns out that they have only a small influence on the final result. The exchange integrals, for instance, seem largely to cancel each other. Actually this approach is quite analogous to the Hartree method of self-consistent fields, which has been found to be a very good approximation for many-electron systems.

A more general treatment is given by Kembe and Van Vleck[6] in a later article about oxygen. There $1/r_{ik}$ is expanded by means of spherical harmonics and the integrals are expressed in the coefficients c_k and the radial integrals F_k and G_k, with the notations of Condon and Shortley. Innes and Ufford[7] have made a similar calculation with tensor operators. The difference, however, between their results and those of Abragam and Van Vleck is - for oxygen - remarkably small. For heavier atoms this method would be extremely complicated and the improvement probably quite negligible in most applications.

We therefore apply the simplified method described above and start to discuss the operator (9) term by term.

Breit-Margenau Correction

The first term of Eq. (9) has the same form as the relativistic mass correction in the single-electron case and needs no furhter treatment.

The second and third term can be written

$$\delta Z_2 = \frac{\mu_B e^2}{8\pi\epsilon_0 mc^2} \sum_i \bar{\sigma}_i \cdot \left[\nabla_i \left(-\frac{Z}{r_i} + \sum_k^{k\neq i} \frac{1}{r_{ik}} \right) \times \bar{A}_i \right]$$

$$= \frac{\mu_B}{2mc^2} \sum_i \sigma_i \cdot \left(\nabla_i V_i \times \bar{A}_i \right) ,$$

where

$$4\pi\epsilon_0 V_i = -\frac{Ze^2}{r_i} + \int \sum_k^{k\neq i} \psi_k^*(\bar{r}') \frac{e^2}{|\bar{r}_i - \bar{r}'|} \psi_k(\bar{r}') \, d\tau'$$

$$= -\frac{Ze^2}{r_i} + \int \frac{e^2}{|\bar{r}_i - \bar{r}'|} \rho_i(\bar{r}') \, d\tau' .$$

If ρ_i is spherically symmetric, V_i becomes exactly the central potential used in the Hartree method, and δZ_2 is therefore just a sum of single-electron spin-orbit corrections, derived in the preceding section.

These two corrections together are called the Breit-Margenau correction or, since they both depend on the kinetic energy, the relativistic correction.

Spin-Other-Orbit or Lamb Correction

In the same way we get for the fourth term of (9)

$$\delta Z_3 = \frac{\mu_B e^2}{4\pi\epsilon_0 mc^2} \sum_i \sum_k^{k\neq i} \bar{\sigma}_i \cdot \left(\nabla_k \frac{1}{r_{ik}} \times \bar{A}_k \right) -$$

$$= \frac{\mu_B e^2}{4\pi\epsilon_0 mc^2} \sum_i \int \bar{\sigma} \cdot \left(\nabla' \frac{1}{|\bar{r}_i - \bar{r}'|} \times \bar{A}' \right) \rho_i(\bar{r}') \, d\tau'$$

(where ∇' implies derivation with respect to primed coordinates).
In the following we drop the subscript i :

$$\nabla' \frac{1}{|\bar{r} - \bar{r}'|} \times A' = - \nabla \times \frac{\bar{A}'}{|\bar{r} - \bar{r}'|}$$

gives

$$\delta Z_3 = - \frac{\mu_B e^2}{4\pi \epsilon_0 mc^2} \sum \bar{\sigma} \cdot rot \int \frac{\bar{A}'}{|\bar{r} - \bar{r}'|} \rho(\bar{r}') d\tau' ,$$

which is exactly the formula Lamb[8] derived classically, assuming an
induced current in the core caused by the electrons in unfilled shells.

If ρ is spherically symmetric it follows from the symmetry that
the integral above is a vector pointing in the direction of $\bar{r}$. We now expand
$1/(\bar{r} - \bar{r}')$ in Legendre polynomials:

$$\frac{1}{|r - r'|} = \sum_{\ell = 0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_{\ell}(\cos \omega) ,$$

where $r_<$ is the smaller and $r_>$ the larger of r and r' and ω is the
angle between $\bar{r}$ and $\bar{r}'$. We get

$$\int \frac{\bar{A}'}{|\bar{r} - \bar{r}'|} \rho(\bar{r}') d\tau' = \frac{1}{2} \bar{B} \times \int \frac{\bar{r}}{|\bar{r} - \bar{r}'|} \rho(\bar{r}') d\tau'$$

and

$$\int \frac{\bar{r}}{|\bar{r} - \bar{r}'|} \rho(\bar{r}') d\tau' = \frac{\bar{r}}{r} \int r' \cos \omega \sum \frac{r_<^{\ell}}{r_>^{\ell+1}} P_{\ell}(\cos \omega) \rho(\bar{r}') r'^2 d\Omega \, dr'.$$

But $\cos \omega = P_1 (\cos \omega)$ and $\int P_\ell (\cos \omega) P_{\ell'} (\cos \omega) d\Omega = \delta(\ell \ell') \frac{4\pi}{2\ell +1}$.

If we introduce the radial density $\rho'(r') = 4\pi r'^2 \rho(\bar{r}')$, we get

$$\frac{e^2}{4\pi \epsilon_0} \int \frac{\bar{r}'}{|\bar{r} - \bar{r}'|} \rho(r') d\tau' = \bar{r} \, Y(r) = \frac{\bar{r}}{3} \left[U(r) + W(r) \right] ,$$

where

$$U(r) = \frac{e^2}{4\pi \epsilon_0 r^3} \int_0^r r'^2 \rho'(r') dr' \quad \text{and} \quad W(r) = \frac{e^2}{4\pi\epsilon_0} \int_r^\infty \frac{\rho'(r')}{r'} dr' .$$

But

$$\nabla \times (\bar{B} \times \bar{r} \, Y) = Y \nabla \times (\bar{B} \times \bar{r}) + \nabla Y \times (\bar{B} \times \bar{r}) = 2 \bar{B} Y - U \frac{\bar{r} \times (\bar{B} \times \bar{r})}{r^2} ,$$

which gives

$$\delta Z_3 = - \frac{\mu_B}{mc^2} \sum \bar{\sigma} \cdot \left[\bar{B} Y - \frac{1}{2} \frac{\bar{r} \times (\bar{B} \times \bar{r})}{r^2} U \right] =$$

$$= - \frac{\mu_B}{mc^2} \bar{B} \cdot \sum \left[\bar{\sigma} Y - \frac{1}{2} \left(\bar{\sigma} - \frac{(\bar{\sigma} \cdot \bar{r})}{r^2} \bar{r} \right) U \right] .$$

Orbit-Orbit correction

The last term of Eq. (9) can be written in a similar way:

$$\delta Z_4 = - \frac{e^3}{8\pi\epsilon_0 m^2 c^2} \sum \bar{p} \left[\int \frac{\bar{A}'}{|\bar{r} - \bar{r}'|} \rho(r') d\tau' + \int \frac{(\bar{r} - \bar{r}') \cdot \bar{A}'}{|\bar{r} - \bar{r}'|^3} (\bar{r} - \bar{r}') \rho(\bar{r}') d\tau' \right] .$$

Now

$$\nabla \left\{ \frac{(\bar{r} - \bar{r}') \cdot \bar{A}'}{|\bar{r} - \bar{r}'|} \rho(r') \right\} = - \frac{(\bar{r} - \bar{r}')}{|\bar{r} - \bar{r}'|^3} (\bar{r} - \bar{r}') \cdot \bar{A} \rho(\bar{r}') + \frac{\nabla [(\bar{r} - \bar{r}') \cdot \bar{A} \rho(\bar{r}')]}{|\bar{r} - \bar{r}'|} ,$$

and

$$\nabla[(\bar{r} - \bar{r}') \cdot \bar{A}' \rho(\bar{r}')] = \rho(\bar{r}')(\bar{A}' \cdot \nabla)(\bar{r} - \bar{r}') = \rho(\bar{r}') \bar{A}' .$$

We shall first show that the integral over the expression in the braces is zero. Let the polar axis of a spherical coordinate system fall along $\bar{r}$ and let $\bar{r}'$ have the coordinates $(r'\theta'|\phi')$ and $\bar{B}$ $(B\,\theta\,\phi)$. Then

$$(\bar{r} - \bar{r}') \cdot \bar{A}' = \frac{1}{2}(\bar{r} - \bar{r}') \cdot (\bar{B}x\bar{r}') = \frac{1}{2}\bar{r} \cdot (\bar{B}x\bar{r}') = \frac{1}{2} rr' B \sin\theta \sin\theta' \sin(\phi'-\phi).$$

When $\frac{1}{|\bar{r} - \bar{r}'|}$ is expanded in Legendre polynomials $P_\ell(\cos\theta')$, it is easily seen that the integral vanishes if ρ is spherically symmetric. Therefore

$$\int \frac{(\bar{r} - \bar{r}') \cdot A'}{|\bar{r} - \bar{r}'|^3}(\bar{r} - \bar{r}') \rho(\bar{r}')\, d\tau' = \int \frac{\bar{A}' \rho(\bar{r}')}{|\bar{r} - \bar{r}'|}\, d\tau' ,$$

and the entire correction becomes

$$\delta Z_4 = -\frac{e}{m^2 c^2} \sum \bar{p} \cdot \int \frac{e^2 \bar{A}' \rho(\bar{r}')}{4\pi \epsilon_0 |\bar{r} - \bar{r}'|}\, d\tau'.$$

The integral was evaluated in the preceding section and is equal to $\frac{1}{2} \bar{B}x\bar{r}\, Y(r)$, where $Y(r)$ is the radial integral defined above. But $\bar{p} \cdot (\bar{B}x\bar{r}) = \hbar\, \bar{B} \cdot \bar{\ell}$, where $\bar{\ell} = \frac{1}{\hbar}\bar{r}x\bar{p}$, and therefore

$$\delta Z_4 = -\frac{\mu_B}{mc^2}\, \bar{B} \cdot \sum \bar{\ell}\, Y .$$

We shall refer to the spin-other-orbit and orbit-orbit corrections as the diamagnetic correction. Only the former was considered by Lamb since he dealt only with s electrons.

Obviously, there is no contribution to the Zeeman energy from the spin-spin interaction, since the latter is independent of the momentum and hence not affected by a magnetic field.

If we now add together all the different terms of the operator (9) we have discussed above, we obtain the following total correction to the classical Zeeman operator:

$$\delta Z = -\mu_B \overline{B} \cdot \sum \left[(\overline{\ell} + \overline{\sigma}) \frac{T+Y}{mc^2} - \left(\overline{\sigma} - \frac{(\overline{\sigma} \cdot \overline{r})}{r^2} \overline{r} \right) \frac{\frac{1}{2} r \cdot \frac{dV}{dr} + U}{2mc^2} \right].$$

(10)

Only electrons outside closed shells contribute in this summation. Except for the radial parts, this operator is exactly the same as in the single-electron case. We therefore get the matrix elements in the $(n \, \ell \, m_s \, m_\ell)$ scheme from Eqs. (6) and (7):

$$\left\langle n\ell \, m_s m_\ell \, \middle| \, \delta Z \, \middle| \, n\ell m_s m_\ell \right\rangle = -\mu_B B \sum \left[(m_\ell + 2m_s) \frac{\langle T+Y \rangle}{mc^2} - m_s \langle \sin^2\theta \rangle \frac{\langle T+U \rangle}{mc^2} \right]$$

(11)

$$\left\langle n\ell \, m_s m_\ell \, \middle| \, \delta Z \, \middle| \, n\ell \, m_s \mp 1 m_\ell \pm 1 \right\rangle =$$

$$= \mu_B B \frac{2m_\ell \pm 1}{2(2\ell - 1)(2\ell + 3)} \left[\ell(\ell+1) - m_\ell(m_\ell \pm 1) \right]^{1/2} \frac{\langle T+U \rangle}{mc^2}.$$

(12)

Here $\langle \sin^2\theta \rangle = 2 \frac{\ell(\ell+1) - 1 + m_\ell^2}{(2\ell-1)(2\ell+3)}$, T is the kinetic energy, $Y = 1/3 (U+W)$,

$U = \frac{e^2}{4\pi\epsilon_0 r^3} \int_0^r r'^2 \rho'(r') dr'$ and $W = \frac{e^2}{4\pi\epsilon_0} \int_r^\infty \frac{\rho(r')}{r'} dr'$, and $\rho'(r')$ is the

radial density of all electrons except that one we are taking the average for $(\int \rho'(r') dr' = Z-1)$. With these formulas we can calculate the corrections for any state that is expressed as a linear combination of single-electron states of the same configuration.

Comparison between the operators (5) and (10) and the Breit-Margenau formula (8) shows that for one electron outside closed shells (or one electron hole) the g-value correction can be written

$$\delta g = - g \frac{\langle T+Y \rangle}{mc^2} - \left[\frac{(j + 1/2)^2}{j(j + 1)} - g \right] \frac{\langle T+U \rangle}{mc^2} =$$

$$= - \frac{3j(j+1) - \ell(\ell+1)+3/4}{2j(j + 1)} \frac{\langle T+Y \rangle}{mc^2} + \frac{j(j+1) - \ell(\ell+1) + 1/4}{2j(j + 1)} \frac{\langle T+U \rangle}{mc^2} ,$$

(13)

which is a generalization of the Breit-Margenau formula, also including the diamagnetic correction.

Equivalent Electrons

The calculations are much simplified if all electrons outside closed shells are equivalent (same n and ℓ). Then the radial parts of the wave function are identical for those electrons which contribute, and Eq. (10) can be written

$$\delta Z = - \mu_B \overline{B} \cdot \frac{T+Y}{mc^2} \sum (\overline{\ell}+\overline{\sigma}) + \mu_B \overline{B} \cdot \frac{\frac{1}{2} r \frac{dV}{dr} + U}{mc^2} \sum \left(\overline{\sigma} - \frac{(\overline{\sigma} \cdot \overline{r})}{r^2} \overline{r} \right).$$

(14)

The first term of (14) is, except for the radial part, identical to the classical Zeeman operator. Its contribution to the g-value correction can therefore be written

$$\delta g' = - g \frac{\langle T + Y \rangle}{mc^2} ,$$

where g is the classical g value. One may note that this holds even if the coupling is not of the Russell-Saunders type. This term is usually the dominating part of (14), and an estimate of the correction can therefore be made from this very simple expression.

The second term in (14) is very similar to the magnetic hfs operator and can be treated in the same way (see Edmonds[9] p. 118).

For the Hund's-rule ground term (maximum S and largest possible L consistent with maximum S), the following general formula for the g-value correction has been given by Judd and Lindgren[10]

$$\delta g = -g\frac{\langle T+Y\rangle}{mc^2} + h\frac{\langle T+U\rangle}{mc^2} ,$$

where

$$h = -\frac{2(2\ell - 2n + 1)}{3n(2\ell-1)(2\ell+3)(2L-1)} \left\{ \frac{L(L+1)[J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)} \right.$$

$$-\frac{3}{4}\frac{[J(J+1) - L(L+1) - S(S+1)][J(J+1) + L(L+1) - S(S+1)]}{J(J+1)} \left. \right\} +$$

$$+ \frac{J(J+1) - L(L+1) + S(S+1)}{3J(J+1)} . \tag{15}$$

Here n is the number of electrons or holes in the unfilled shell, whichever is the smaller. This formula is valid for any J in this term. For J = L + S it reduces to

$$\delta g = -g\frac{\langle T+Y\rangle}{mc^2} + n\frac{12\ell(\ell+1) - 3n(2\ell+1) + 2n^2 - 5}{6J(2\ell-1)(2\ell+3)}\frac{\langle T+U\rangle}{mc^2} .$$

$$\tag{16}$$

Application to Thulium

The electronic ground state of thulium has been determined optically and is, with spectroscopic notations, $4f^{13} 6s^2$, $^2F_{7/2}$. Since the configuration consists of a single hole in completely filled shells, the ground state can be expected to be very pure. Futhermore, the electrostatic interaction can mix only states with the same S, L, and J and hence has no effect on the g value. The configuration interaction caused by the spin-orbit coupling can be shown to be quite negligible. Therefore any measurable deviation of the g value from the Landé value must be caused by (a) the anomalous moment of the electron and (b) relativistic and diamagnetic effects.

The experimental g value of thulium has been measured with the atomic-beam technique for the radioactive isotope Tm^{170} (129d) as 1.14122 ± 0.00015.[11] The Landé value including Schwinger correction is 1.14319. The difference, 0.00197 ± 0.00015, is far beyond the experimental uncertainty.

Applying formula (13), we get

$$\delta g = - \alpha^2 \left[\frac{8}{7} \left\langle T+Y \right\rangle - \frac{8}{63} \left\langle T+U \right\rangle \right] = - \alpha^2 \left[\frac{64}{63} \left\langle T \right\rangle + \frac{8}{7} \left\langle Y \right\rangle - \frac{8}{63} \left\langle U \right\rangle \right].$$

Here α is the fine-structure constant, and the radial integrals are expressed in atomic units (see Appendix II).

The radial integrals have been evaluated by use of a pure hydrogenic and a modified hydrogenic wave function (see Appendix I). These wave functions are adjusted to give, together with the Thomas-Fermi potential the experimental value of the spin-orbit coupling constant, which in this case has been determined optically ($\zeta = 2506 \ cm^{-1}$). The following values are then obtained:

I. Hydrogenic wave function:
$\left\langle T \right\rangle = 30.7$, $\left\langle U \right\rangle = 19.2$ and $\left\langle Y \right\rangle = 15.9$ au

II. Modified hydrogenic wave function:

(a) $\kappa = 0.40$,
$\left\langle T \right\rangle = 24.7$, $\left\langle U \right\rangle = 16.5$ and $\left\langle Y \right\rangle = 13.3$.

(b) $\kappa = 0.44$
$\left\langle T \right\rangle = 23.3$, $\left\langle U \right\rangle = 15.6$, $\left\langle Y \right\rangle = 12.5$.

The corrections are summarized in the following table.

	Wave Functions		
	Hydrogenic ($\kappa = 0$)	Modified hydrogenic	
		$\kappa = 0.40$	$\kappa = 0.44$
Landé value	1.14286	1.14286	1.14286
Schwinger correction	+0.00033	+0.00033	+0.00033
Breit-Margenau correction	-0.00166	-0.00134	-0.00127
Diamagnetic correction	-0.00084	-0.00070	-0.00066
Theoretical value	1.14069	1.14115	1.14126
Experimental value		1.14122 ± .00015	

It is seen from this table that the hydrogenic wave function gives a correction that is significantly too large, whereas the modified wave function, which has a shape very close to the Hartree functions, gives excellent agreement with the experiment.

Remarks

The experimental g value together with the spin-orbit coupling parameter can be considered as a measure of the shape of the radial wave function. It is seen from the above that for thulium this is a strong support of the shape obtained by the self-consistent field (SCF) method. Therefore, wave functions determined in the way described in Appendix I can be expected to be quite reliable in the whole rare earth region. Particularly, the values of $\langle r^{-3} \rangle$ obtained from these wave functions should be quite accurate, which is of great importance for the determination of nuclear moments from hyperfine-structure measurements.

For thulium the following values of $\langle r^{-3} \rangle$ are obtained: 10.6 au for $\kappa = 0.40$ and 10.4 au for $\kappa = 0.44$, while a hydrogenic wave function ($\kappa = 0$) gives 11.3 au. It should be emphasized that the hydrogenic wave function used here has been fitted to the experimental spin-orbit coupling by using the Thomas-Fermi potential rather than the very crude formula

$$\zeta = hc\, R_y\, a^2\, \frac{Z_{eff}^4}{n^3 \ell\, (\ell+1/2)\, (\ell+1)} \tag{17}$$

which has been frequently used by spectroscopists. If the effective nuclear charge Z_{eff} is determined from this formula, the hydrogenic wave function gives a g-value correction which is even much larger than in the case shown above and consequently in very poor agreement with the experiment. This disagreement makes the values of $\langle r^{-3} \rangle$ calculated by means of Eq. (17) highly questionable. For thulium this would give $Z_{eff} = 32.8$ and $\langle r^{-3} \rangle = 13.1$ au which is about 25% greater than the value obtained with the modified wave function above. This means that nuclear moments determined by use of Eq. (17) also might suffer from an error of the same order of magnitude.

Appendix I

Analytic Radial Wave Functions

The best radial wave functions that can be obtained at present are the SCF wave functions of Hartree or Hartree-Foch type. For numerical calculations it is very convenient to have analytic approximations of these functions, which also enable us to interpolate and extrapolate between existing functions. A suitable form is the Slater-Löwdin[12] approximation, which for a function of the 4f type (single maximum) is

$$R(r) = r^n (c_1 e^{-a_1 r} + c_2 e^{-a_2 r} + c_3 e^{-a_3 r} + \cdots) .$$

This is a generalization of the hydrogenic form $R(r) = N r^n e^{-ar}$. With three terms in this expansion the agreement with the original function is extremely good. For our purpose, however, we prefer to use a two-parameter wave function, and choose the symmetric form

$$R(r) = Nr^n e^{-ar} \cosh \kappa(ar-n) = \frac{1}{2} Nr^n \left[e^{-\kappa n} e^{-a(1-\kappa)r} + e^{\kappa n} e^{-a(1+\kappa)r} \right] .$$

$$(A-1)$$

For this function the position of the maximum depends only on a ($r_{max} = \frac{n}{a}$), and the other parameter, κ determines essentially the shape. One could easily determine both parameters in Eq. (A-1) by interpolation or extrapolation from existing SCF calculations, but more reliable wave functions are probably obtained if one of the parameters is determined from the experimental spin-orbit coupling constant. Since the shape of the wave function differs very little from element to element, we determine κ by comparing with SCF wave functions and a from the spin-orbit coupling. For the calculation of the spin-orbit coupling the Thomas-Fermi potential is accurate enough. In fact, comparison with SCF calculations shows that the Thomas-Fermi potential is a very good approximation for heavy atoms, particularly near the nucleus, where the main contribution to the spin-orbit coupling comes from (see Fig. 1).
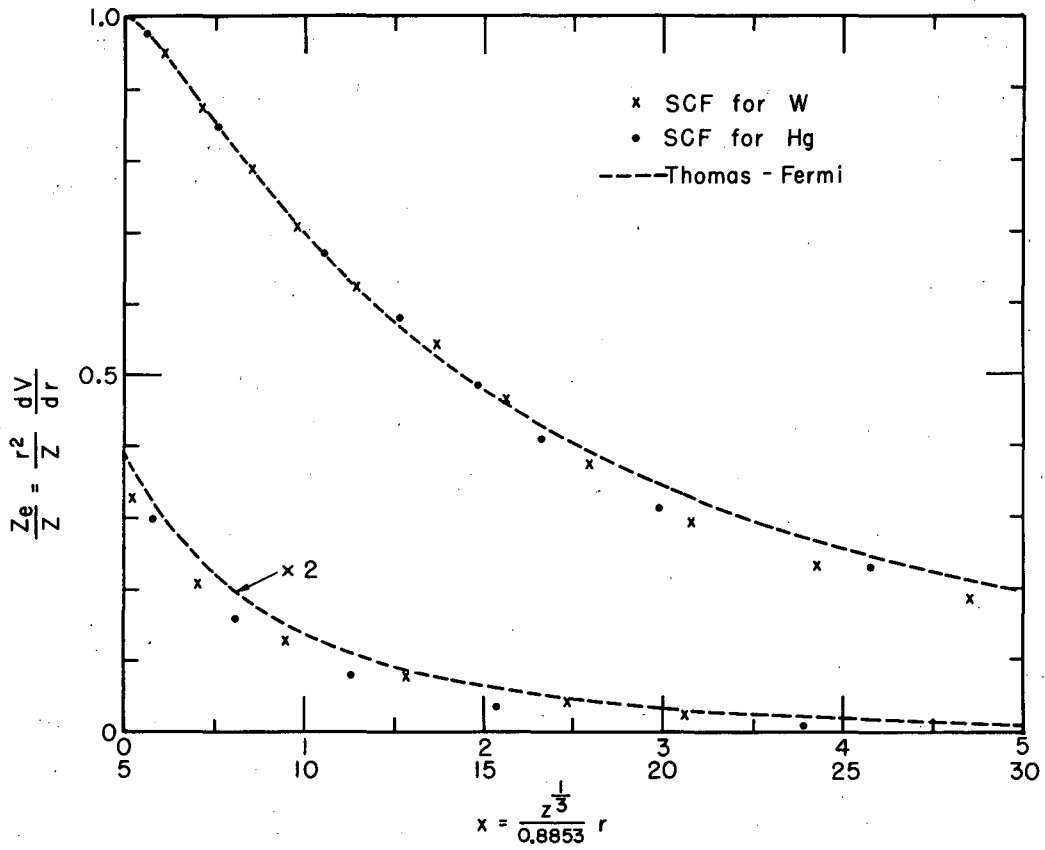
Fig. 1. Comparison between $r^2 \dfrac{dV}{dr}$ from Thomas-Fermi and from self-consistent fields.

No SCF calculations are available for any rare earth atoms, but some have recently been carried out for Pr^{3+} and Tm^{3+} by Ridley. The difference in shape (κ value) between the 4f wave functions for these ions is very small. Since one would not expect the shape to differ much between the ions and the atoms, an accurate value of κ can be obtained from these functions. One can also estimate the κ value by extrapolating from the heavier atoms W and Hg. Figures 2-4 show the four SCF wave functions mentioned above and their approximations according to Eq. (A-1). For comparison the best hydrogenic approximations are also given. The most reasonable value of κ for the thulium atom determined in this way is about 0.4 or slightly more. One should here keep in mind that all functions we want to average are decreasing with r, which means that the part nearest the nucleus is most important, while the shape of the long tail is uncritical.

For the wave function (A-1) the following formulas are easily verified:

(subscript hy indicates hydrogenic value with the same value of a)

$$N^2 = \frac{(2a)^{2n+1}}{(2n)!} \frac{1}{C_{2n+1}} = \frac{N^2_{hy}}{C_{2n+1}} \quad ,$$

$$\left\langle r^{-m} \right\rangle = \frac{(2n-m)!\,(2a)^m}{(2n)!} \frac{C_{2n+1-m}}{C_{2n+1}} = \left\langle r^{-m} \right\rangle_{hy} \frac{C_{2n+1-m}}{C_{2n+1}} \quad ,$$

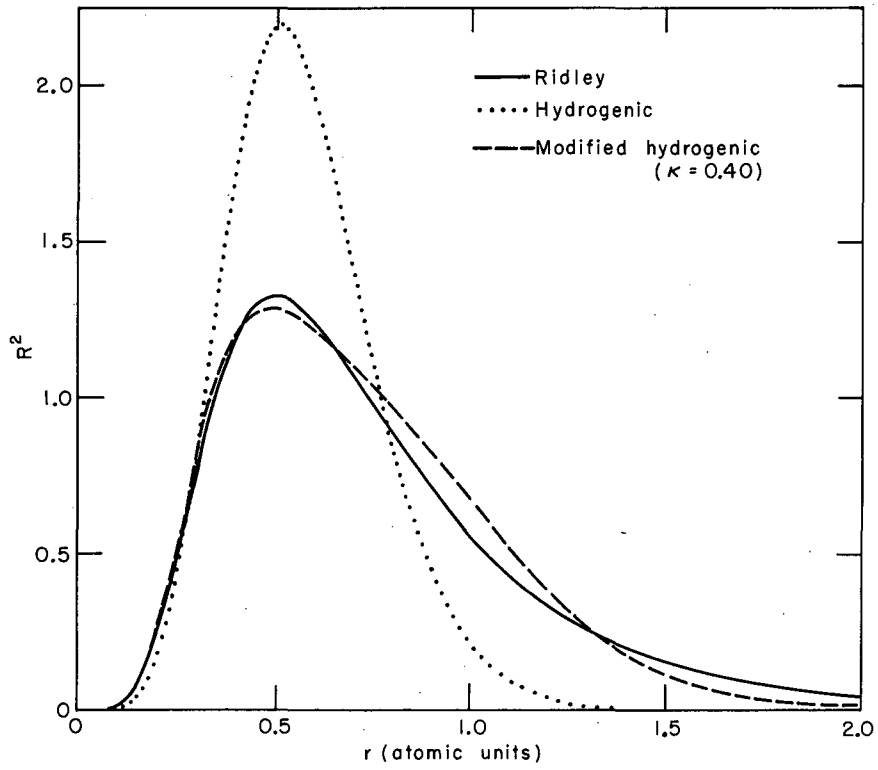where $C_s = \frac{1}{4} \left[e^{-2n\kappa} (1-\kappa)^{-s} + 2 + e^{2n\kappa} (1+\kappa)^{-s} \right]$;

$$\left\langle r^{-m} \tanh \kappa(ar-n) \right\rangle = \left\langle r^{-m} \right\rangle_{hy} \frac{D_{2n+1-m}}{C_{2n+1}} \quad ,$$

where $D_s = \frac{1}{4} \left[e^{-2n\kappa} (1-\kappa)^{-s} - e^{2n\kappa} (1+\kappa)^{-s} \right]$;
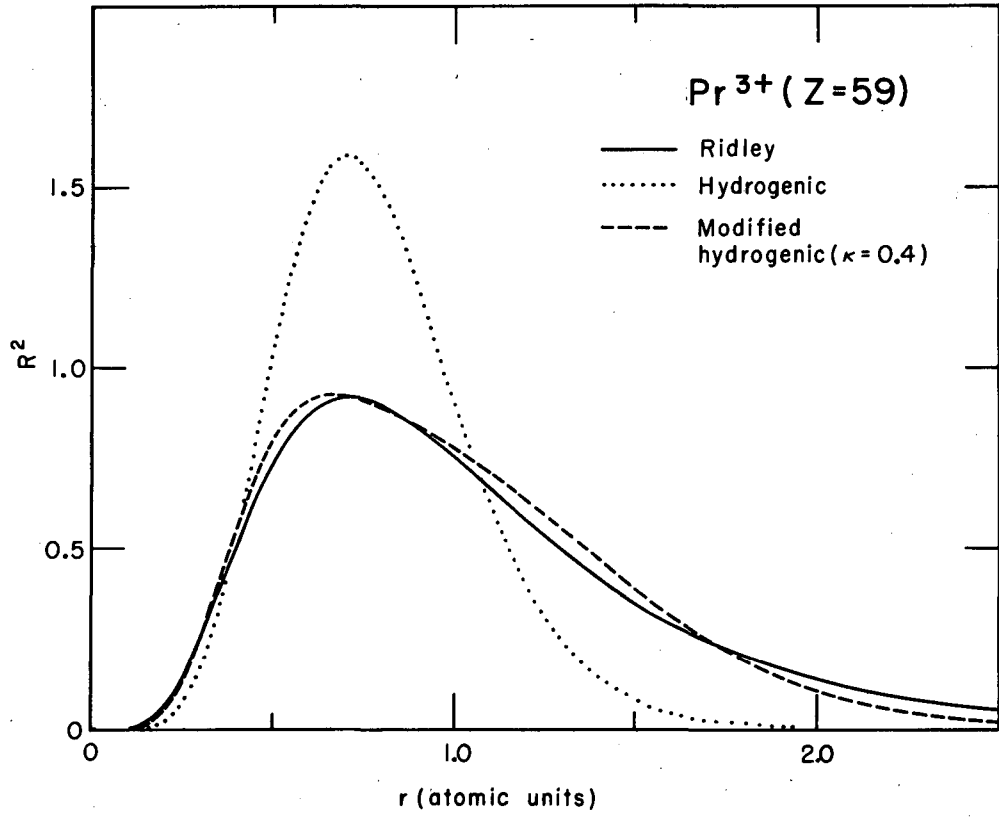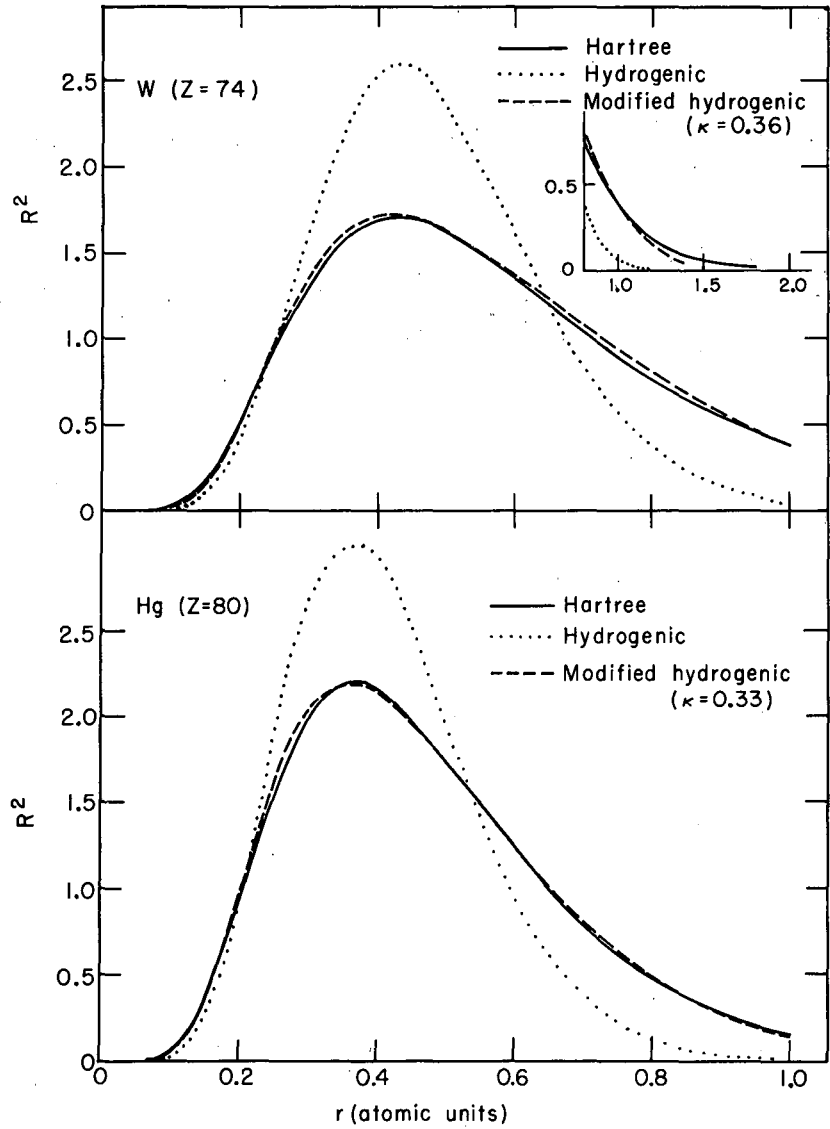
Fig. 2. Radial wave functions for Pr^{3+} .

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Fig. 3. Radial wave functions for Tm^{3+}.

Fig. 4. Radial wave functions for W and Hg.

$$C_s + \kappa D_{s+1} = C_{s+1}$$

$$\frac{1}{R} \frac{d^2R}{dr^2} = \frac{n(n-1)}{r^2} - \frac{2na}{r} + (1+\kappa^2) a^2 + 2\kappa a \left(\frac{n}{r} - a \right) \tanh \kappa (ar-n)$$

gives $\dfrac{\langle T \rangle}{mc^2} = \dfrac{a^2}{2} \left[n(n-1) \left\langle \dfrac{1}{r^2} \right\rangle - \left\langle \dfrac{1}{R} \dfrac{d^2R}{dr^2} \right\rangle \right] = \dfrac{1}{2} a^2 a^2 \left[1 - \kappa^2 - 2\kappa \dfrac{D_{2n}}{C_{2n+1}} \right].$

Appendix II

Atomic Units

Formulas in atomic physics can be considerably simplified by the use of basic units that are directly related to the fundamental constants. The most frequently used atomic unit system was introduced by Hartree and is based on the following units:

m_e , mass of electron $\qquad\qquad\qquad\qquad\left[kg \right]$

e , charge of electron $\qquad\qquad\qquad\qquad\left[As \right]$

$\hbar$, Planck's constant divided by 2π $\qquad\left[kg\ m^2/s \right]$

$4\pi\epsilon_0$, 4π times the permittivity of free space $\qquad\left[A^2 s^4/kgm^3 \right]$.

The dimensions are given in MKSA units in the square brackets. From these one can easily get the units of other quantities; e.g.,

unit of length $\left[m \right]$: $\dfrac{4\pi\epsilon_0\ \hbar^2}{m_e\ e^2} = a_0$ (first Bohr radius);

unit of velocity $\left[m/s \right]$: $\dfrac{e^2}{4\pi\epsilon_0 \hbar} = \alpha c$ (α is fine-structure

constant, c is velocity of light) ;

unit of energy $\left[kg\ m^2/s^2 \right]$: $\dfrac{m_e\ e^4}{(4\pi\epsilon_0)^2\hbar^2} = 2hc\ R_y$ (R_y is Rydberg's

constant);

unit of magnetic moment $\left[Am^2 \right] := \dfrac{e\hbar}{m_e} = 2\mu_B$ (μ_B is Bohr magneton);

unit of permeability $\left[\dfrac{\text{kg m}}{\text{A}^2\text{s}^2}\right]$: $\dfrac{4\pi\epsilon_0\hbar^2}{e^4} = \dfrac{1}{a^2}\dfrac{\mu_0}{4\pi}$ (μ_0 is

permeability of free space).

General formulas (with correct dimensionality) are directly transformed to atomic units by replacing m_e, e, $\hbar$, a_0, and $4\pi\epsilon_0$ by unity, c by $1/a$, $\dfrac{\mu_0}{4\pi}$ by a^2, μ_B and $hc\,R_y$ by $1/2$, etc.; e.g.,

(a) Spin-Orbit coupling

$$\zeta = \frac{1}{4\pi\epsilon_0}\frac{\hbar^2}{2m_e^2c^2}\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle = \frac{\mu_0}{4\pi}2\mu_B^2\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle =$$

$$= hc\,R_y\,a^2\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle$$

becomes $\zeta = \dfrac{1}{2}a^2\left\langle\dfrac{1}{r}\dfrac{dV}{dr}\right\rangle$ in atomic units.

(b) Magnetic dipole coupling

$$ha = \frac{\mu_0}{4\pi}\mu_B^2\,g_I\,\frac{2\ell(\ell+1)}{j(j+1)}\left\langle\frac{1}{r^3}\right\rangle = hc\,R_y\,a^2\,g_I\,\frac{\ell(\ell+1)}{j(j+1)}\left\langle\frac{a_0^3}{r^3}\right\rangle$$

becomes $ha = \dfrac{1}{2}a^2\,g_I\,\dfrac{\ell(\ell+1)}{j(j+1)}\left\langle\dfrac{1}{r^3}\right\rangle$.

(c) Electric quadrupole coupling

$$hb = \frac{e^2Q}{4\pi\epsilon_0}\frac{2j-1}{2(j+1)}\left\langle\frac{1}{r^3}\right\rangle = 2\,hc\,R_y\,\frac{Q}{a_0^2}\frac{2j-1}{2(j+1)}\left\langle\frac{a_0^3}{r^3}\right\rangle$$

becomes $hb = Q\,\dfrac{2j-1}{2(j+1)}\left\langle\dfrac{1}{r^3}\right\rangle$.

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