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Modified delta-function potential for hyperfine interactions

S. M. Blinder
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

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A modification of the Fermi contact interaction is proposed in which the nuclear moment is represented by a uniformly magnetized spherical shell of radius r_0. In effect, the delta function $\delta(r)$ in the Fermi Hamiltonian is replaced by $\delta(r-r_0)$. The Schrödinger equation for a hydrogenlike system thus perturbed is exactly solvable in terms of the Coulomb Green's function. Negative energy eigenvalues have the form $E_\nu = -Z^2/2\nu^2$, with ν a nonintegral quantum number. An asymptotic formula is derived for the quantum defect $\delta = \nu - n$. The $l=0$ eigenfunctions are multiples of the Whittaker functions: $M_{\nu,}^{1/2}(2Zr/\nu)$ for $r<r_0$ and $W_{\nu,}^{1/2}(2Zr/\nu)$ for $r>r_0$. Explicit forms are given by expansion of the Whittaker functions to first order in quantum defect. In the limit $r_0 \rightarrow 0$ results pertaining to the original Fermi Hamiltonian are approached. It is shown that a repulsive delta function maintains the unperturbed Coulomb energy while an attractive delta function pulls all bound state energies to $-\infty$. Perturbation expansions are discussed and comparisons made with earlier calculations. It is shown that second-order and higher perturbation energies diverge as $r_0 \rightarrow 0$.

I. INTRODUCTION

The interaction between a nuclear magnetic moment and an atomic s electron is most simply represented by the Fermi contact operator[1]

$$\mathcal{H}' = \frac{8\pi}{3} g g_I \mu_B \mu_N \vec{s} \cdot \vec{I} \delta^3(\vec{r}), \quad \delta^3(\vec{r}) = \delta(r)/4\pi r^2 . \tag{1}$$

This operator in first-order perturbation theory accounts quite accurately for atomic hyperfine splittings. For hydrogenlike systems[2]:

$$E^1_{n,F} = \tfrac{8}{3}\pi g g_I \mu_B \mu_N (\vec{s}\cdot\vec{I})_F |\psi_n(0)|^2, \quad \vec{F} = \vec{I} + \vec{s},$$
$$F = I \pm \tfrac{1}{2}, \quad (\vec{s}\cdot\vec{I})_F = \tfrac{1}{2}[F(F+1) - s(s+1) - I(I+1)], \tag{2}$$

$$|\psi_n(0)|^2 = Z^2/\pi n^3 a^3, \quad a \equiv \hbar^2/\mu e^2, \quad \mu = m(1+m/M)^{-1}.$$

The hyperfine splitting is given by

$$\hbar \Delta\nu^{(1)} = E^{(1)}_{n,I+1/2} - E^{(1)}_{n,I-1/2} = \lambda Z^3 (I + \tfrac{1}{2})/n^3, \quad \lambda \equiv \tfrac{8}{3} g g_I \mu_B \mu_N / a^3 . \tag{3}$$

For $1s$ atomic hydrogen ($Z=1$, $n=1$, $I=\frac{1}{2}$) the first-order perturbation calculation gives[3]

$$\Delta\nu^{(1)} = \lambda/h = 1420.4847 \text{ MHz} \tag{4}$$

compared with the experimental value[4]

$$\Delta\nu = 1420.405\,751\,7680(15) \text{ MHz}. \tag{5}$$

Better agreement can be attained, of course, when relativistic, radiative, and nuclear structure corrections are taken into account.[2]

The Fermi operator is usable, however, only to first order. Second-order perturbation energies for a δ-function potential diverge to $-\infty$ for s states.[5] This singularity has led to difficulties in calculations of nuclear spin-spin coupling constants in molecules, notably HD.[6] Divergence of second-order perturbation energies can be circumvented by replacing the δ-function in (1) by a less singular function. Let the operator interaction be accordingly represented in the form

$$\mathcal{H}' = \lambda_F (\pi a^3/4\pi r^2) \Delta(r), \quad \lambda_F \equiv \lambda (\vec{s}\cdot\vec{I})_F . \tag{6}$$

For the Fermi operator itself,

$$\Delta^F(r) = \delta(r). \tag{7}$$

The author has shown some time ago, by reduction of the Coulomb Dirac equation in the field of a point nuclear magnetic dipole, that the function Δ is more correctly represented as[7]

$$\Delta^B(r_0, r) = r_0/(r+r_0)^2, \quad r_0 \equiv Ze^2/2mc^2 . \tag{8}$$

Power and Pitzer[8] applied this operator in a second-order perturbation calculation for atomic hydrogen. Gregson, Hall, and Rees[9] suggested an approximation to (8) of the form

$$\Delta^{\text{GHR}}(r_0, r) = e^{-r/r_0}/r_0 . \tag{9}$$

Both the Blinder and the Gregson-Hall-Rees operators have been employed in calculations of the spin-spin coupling in HD.[10] Further discussion of the Blinder operator has appeared in several recent publications.[11]

In this paper I shall present an alternative model for the Fermi contact interaction, to be known as the *modified Fermi potential*. It will be shown that the modified Fermi potential leads to a Schrödinger equation which is *exactly* solvable. Thus the pitfalls inherent in perturbation expansions can be avoided entirely. Our analysis will also reveal the explicit origin of the divergences produced by the usual δ-function potential. In a projected application of the results of this paper, nuclear spin-spin coupling can be reduced to a *first-order* perturbation effect, without the complication of divergent self-interactions.[12]

II. MODIFIED FERMI POTENTIAL

In the model which I propose, the nuclear moment is represented by a uniformly magnetized spherical shell of radius r_0. This corresponds to a Δ operator of the form:

$$\Delta^{\mathrm{MF}}(r_0, r) = \delta(r - r_0). \tag{10}$$

In common with (8) and (9), the modified Fermi potential (10) reduces in the limit $r_0 \to 0$ to the usual Fermi δ function, viz.,

$$\lim_{r_0 \to 0} \Delta(r_0, r) = \delta(r). \tag{11}$$

A hydrogenlike atom perturbed by a modified Fermi potential is represented by the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} + \frac{8\pi}{3} g g_I \mu_B \mu_N \vec{s} \cdot \vec{I} \frac{\delta(r - r_0)}{4\pi r_0^2}\right)\psi(r) = E\psi(r). \tag{12}$$

We shall limit our consideration to s states since, in any event, dipolar and orbital magnetic interactions are dominant for $l > 0$. It is convenient to use the modified atomic units $\hbar = e = \mu = 1$, $\mu \equiv m(1 + m/M)^{-1}$. In terms of the radial function

$$P(r) \equiv (4\pi)^{1/2} r\psi(r) \tag{13}$$

and the wave number k, such that

$$E = \tfrac{1}{2}k^2, \tag{14}$$

the Schrödinger equation can be expressed

$$\left(k^2 + \frac{\partial^2}{\partial r^2} + \frac{2Z}{r}\right)P(r) = \frac{\lambda_F}{2r_0^2} P(r_0)\delta(r - r_0). \tag{15}$$

The parameter λ_F can be either positive or negative, depending on the sign of the nuclear g factor and on the spin expectation value. For atomic hydrogen, $F = 0$ or 1, $\lambda_1 = \frac{1}{4}\lambda$, $\lambda_0 = -\frac{3}{4}\lambda$. Expressed in atomic units,

$$\lambda = \frac{ha}{e^2}\Delta\nu^{(1)} = \frac{8}{3} g g_I \frac{\mu_B \mu_N}{e^2 a^2} = 2.160\,0708 \times 10^{-7}. \tag{16}$$

We observe now that (15) is isomorphic with the defining relation for the S-wave Coulomb Green's function[13,14]:

$$\left(k^2 + \frac{\partial^2}{\partial r^2} + \frac{2Z}{r}\right) g(r, r_0, k) = \delta(r - r_0),$$
$$g(r, r_0, k) \equiv r r_0 G_0(r, r_0, k). \tag{17}$$

The boundary conditions imposed on (17) are

$$r^{-1/2} g(r, r_0, k) \to 0, \quad r^{1/2}\frac{\partial g}{\partial r} \to 0 \quad \text{as } r \to 0 \tag{18}$$

and

$$g(r, r_0, k) \to 0, \quad \frac{\partial g}{\partial r} \to 0 \quad \text{as } r \to \infty \tag{19}$$

which are appropriate as well to the Schrödinger equation (15). Therefore the latter must have solutions of the form

$$P(r) = (\lambda_F / 2r_0^2) P(r_0) g(r, r_0, k) \tag{20}$$

provided only that k does not lie in the unperturbed Coulomb eigenvalue spectrum. The appropriate Green's function is given by[14] (cf. Appendix A)

$$g(r, r_0, k) = (2ik)^{-1}\Gamma(1 - i\nu) M_{i\nu}^{1/2}(-2ikr_<)$$
$$\times W_{i\nu}^{1/2}(-2ikr_>), \tag{21}$$

in which $r_<$ and $r_>$ are, respectively, the lesser and greater of the variables r and r_0,

$$\nu \equiv Z/k, \tag{22}$$

and M and W are Whittaker functions as defined by Buchholz.[15]

Since we shall be concerned with negative-energy solutions to (15), it is expedient to make the replacements

$$-ik \to k, \quad i\nu \to \nu; \quad \mathrm{Re}\,k > 0, \quad \mathrm{Re}\,\nu > 0.$$

The relationship (22) is preserved but now

$$E = -\tfrac{1}{2}k^2 = -Z^2/2\nu^2. \tag{23}$$

The Green's function is accordingly rewritten as

$$g(r, r_0, k) = -(2k)^{-1}\Gamma(1 - \nu) M_\nu(2kr_<) W_\nu(2kr_>). \tag{24}$$

Since we shall encounter only Whittaker functions of order $\frac{1}{2}$, the second index will be suppressed.

The exact eigenfunctions of the Schrödinger equation (15) are therefore given by

$$P_\nu(r) = -\frac{\lambda_F}{4kr_0^2} P_\nu(r_0)\Gamma(1 - \nu) M_\nu(2kr_<) W_\nu(2kr_>). \tag{25}$$

The eigenvalues (23) have the same form as those for the unperturbed Coulomb problem except that the quantum numbers ν are nonintegral when $\lambda_F \neq 0$. From the properties of Green's functions it follows that $P_\nu(r)$ is continuous across r_0 but that its first derivative exhibits a finite discontinuity consistent with

$$\frac{P_\nu'(r_0 + 0) - P_\nu'(r_0 - 0)}{P_\nu(r_0)} = \frac{\lambda_F}{2r_0^2}. \tag{26}$$

The last condition is reflected in the Wronskian of the pair of Whittaker functions,[16]

$$\mathcal{W}\{W_\nu(z), M_\nu(z)\} = 1/\Gamma(1 - \nu). \tag{27}$$

The eigenvalues are determined by a transcendental equation obtained by setting $r = r_0$ in (25). This can be expressed as

$$1 = \lambda_F Z \Gamma(-\nu) M_\nu(z) W_\nu(z)/z^2, \quad z \equiv 2kr_0 = 2Zr_0/\nu . \tag{28}$$

Note that ν (or k) depends on the spin quantum number F and the shell radius r_0. No further reduction of (28) is possible in the general case. We may, however, exploit the fact that physically interesting values of r_0 will lie in the range of about 1 fm (10^{-13} cm), many orders of magnitude smaller than the Bohr radius (1 fm $= 1.8897 \times 10^{-5} a_0$). It is therefore quite adequate (except in one instance discussed below) to approximate the Whittaker functions in (28) by their $z \to 0$ asymptotic forms. From formulas given in Buchholz[17]

$$\begin{aligned} M_\nu(z) &= z e^{-z/2} {}_1F_1(1-\nu; 2; z) \\ &= z e^{-z/2}[1 + \tfrac{1}{2}(1-\nu)z + O(z^2)] \\ &= z[1 - \tfrac{1}{2}\nu z + O(z^2)] , \end{aligned} \tag{29}$$

$$\begin{aligned} \Gamma(-\nu) W_\nu(z) &= M_\nu(z) \ln z + H_\nu(z) , \\ H_\nu(z) &= z e^{-z/2}\{-1/\nu z + [\psi(1-\nu) + \psi(1) + \psi(2)] \\ &\quad + \tfrac{1}{2}(1-\nu)[\psi(2-\nu) + \psi(2) + \psi(3)]z + O(z^2)\} , \end{aligned} \tag{30}$$

where[18]

$$\psi(x) \equiv \frac{d \ln \Gamma(x)}{dx}, \quad \psi(1+x) = \psi(x) + 1/x, \quad \psi(1) = -\gamma, \tag{31}$$

$$\psi(n) = H_{n-1} - \gamma, \quad \gamma \equiv 0.5772\cdots, \quad H_n \equiv 1 + \tfrac{1}{2} + \cdots + 1/n .$$

Therefore (28) can be approximated by

$$\begin{aligned} 1/\lambda_F Z \approx& -1/\nu z + \ln z + \psi(1-\nu) + 2\gamma \\ &+ (1-\nu)/2\nu - \nu\psi(1-\nu)z + O(z) . \end{aligned} \tag{32}$$

Since we are dealing with an exceedingly small perturbation on the Coulomb system ($\lambda \sim 10^{-7}$ in hydrogen), the quantum number ν should differ only minutely from an integer. It is useful to define a quantum defect such that

$$\nu \equiv n + \delta, \quad n = 1, 2, \ldots . \tag{33}$$

In terms of the quantum defect, the energy is given by

$$E_{n,F} = -\frac{Z^2}{2(n+\delta_{n,F})^2} = -\frac{Z^2}{2n^2} + \frac{Z^2}{n^3}\delta_{n,F} - \frac{3Z^2}{2n^4}\delta_{n,F}^2 + \cdots , \tag{34}$$

and the hyperfine splitting by

$$h\Delta\nu_n = E_{n,I+1/2} - E_{n,I-1/2} = \frac{Z^2}{n^3}(\delta_{n,I+1/2} - \delta_{n,I-1/2}) + O(\delta^2) . \tag{35}$$

For hydrogen, the experimental value (5) implies $\delta_1 - \delta_0 = 2.159\,9509 \times 10^{-7}$.

For $\delta \ll 1$,

$$\psi(1-\nu) = 1/\delta + H_{n-1} - \gamma + O(\delta) . \tag{36}$$

Substituting (36) into (32), dropping the indicated first-order terms, and solving for δ, we obtain, with $\rho \equiv 2Zr_0/n$,

$$\delta_{n,F} \approx \frac{\lambda_F Z(1 - n\rho)}{1 + \lambda_F Z(1/n\rho - \ln\rho - H_n + (n+1)/2n - \gamma)} . \tag{37}$$

An alternative derivation is given in Appendix C. If $r_0 \gg \frac{1}{2}\lambda_F$,

$$\delta_F \approx \frac{\lambda_F Z(1 - n\rho)}{1 + \lambda_F Z/n\rho} = \frac{\lambda_F Z(1 - 2Zr_0)}{1 + \lambda_F/2r_0} , \tag{38}$$

the quantum defect being independent of n to this level of approximation.

III. LIMITING BEHAVIOR AS $r_0 \to 0$

The limit $r_0 \to 0$ represents a reduction to the original Fermi contact interaction. Velenik *et al.*[19] carried out variational calculations for a hydrogen atom perturbed by a δ-function potential. They concluded that, for a repulsive δ function ($\lambda_F > 0$ in our notation), the energy maintains its unperturbed Coulomb value while for an attractive δ function ($\lambda_F < 0$), the energy diverges to $-\infty$. A variational calculation on so singular an eigenvalue equation is perhaps suspect.[20,21] Nonetheless, as we shall demonstrate, the conclusions thus arrived at are correct.

Consider first the case $\lambda_F > 0$. As $r_0 \to 0$, Eq. (37) converges uniformly to zero. For $r_0 \ll \frac{1}{2}\lambda_F$,

$$\delta_{n,F} \approx 2Zr_0 . \tag{39}$$

Thus, as $r_0 \to 0$, $\nu \to n$ and the energy approaches its unperturbed value. Figure 1 represents the quantum defect as a function of r_0 for the $F=1$ state of hydrogen.

For $\lambda_F < 0$, (37) likewise applies so long as r_0 is not too close to the value $\frac{1}{2}|\lambda_F|$. The quantum defect increases sharply in the vicinity of $r_0 = \frac{1}{2}|\lambda_F|$. Equation (37) becomes invalid since it was based on the condition $|\delta| \ll 1$. For $r_0 \lesssim \frac{1}{2}|\lambda_F|$, we must revert to Eq. (32), which assumes only that $z \ll 1$.[22] Figure 2 shows the quantum defect for the $F=0$ state of hydrogen. The steep change occurs near $r_0 = 4.29 \times 10^{-3}$ fm, corresponding to $\lambda_0 = -1.6200 \times 10^{-7}$. The quantum number plummets from $\nu = 0.9999$ ($\delta = -1 \times 10^{-4}$) at $r_0 = 4.2932 \times 10^{-3}$ fm to $\nu = 0.0001$ at $r_0 = 4.2828 \times 10^{-3}$ fm. The dependence of ν on r_0 for the $F=0$ state of hydrogen is shown in Fig. 3.

As ν approaches zero, the condition $z = 2Zr_0/\nu \ll 1$, upon which (32) is based, will eventually be

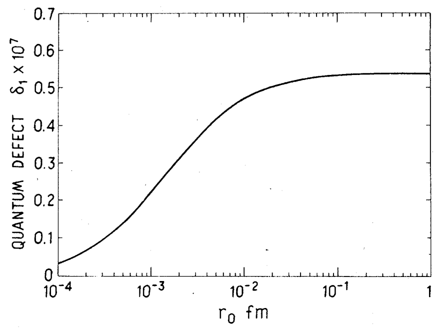

FIG. 1. Quantum defect for the hydrogen 1s, $F=1$ state.

violated. However, as $\nu\to 0$ in (28), the Whittaker functions become spherical Bessel functions. Specifically,[23]

$$M_0(z)=2\sinh(\tfrac{1}{2}z)=e^{z/2}-e^{-z/2},$$
$$W_0(z)=e^{-z/2}. \tag{40}$$

Moreover, for $\nu\approx 0$, $\Gamma(-\nu)\approx -1/\nu$, so that (23) is approximated by

$$1\approx -\frac{\lambda_F Z}{\nu}\,\frac{1-e^{-z}}{z^2},\quad z=\frac{2Zr_0}{\nu}. \tag{41}$$

This is physically meaningful only when $\lambda_F<0$. For $z\ll 1$, (41) reduces to

$$\nu\approx\frac{Zr_0}{1+2r_0/\lambda_F}\quad(\lambda_F<0,\ 1\gg\nu\gg 2Zr_0), \tag{42}$$

which also follows from (32) with $\nu\approx 0$. For $z\gg 1$, on the other hand, (41) implies

$$\nu\approx\frac{4Zr_0^2}{|\lambda_F|}\quad(\lambda_F<0,\ r_0\ll\tfrac{1}{2}|\lambda_F|), \tag{43}$$

such that $z\approx|\lambda_F|/2r_0$. The limit $z\to\infty$ thus corresponds to $r_0\to 0$. Equation (43) shows finally that $\nu\to 0$ as $r_0\to 0$ for $\lambda_F<0$ and, by virtue of (23), $E_\nu\to -\infty$ for all bound s states.

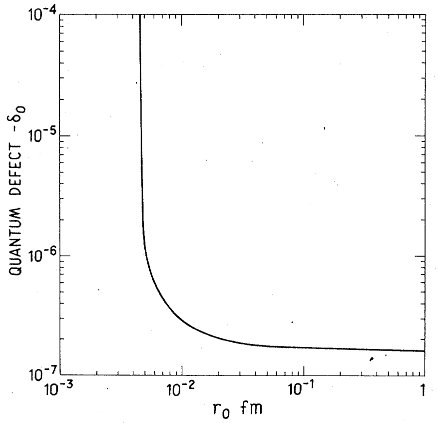

FIG. 2. Quantum defect for the hydrogen 1s, $F=0$ state.

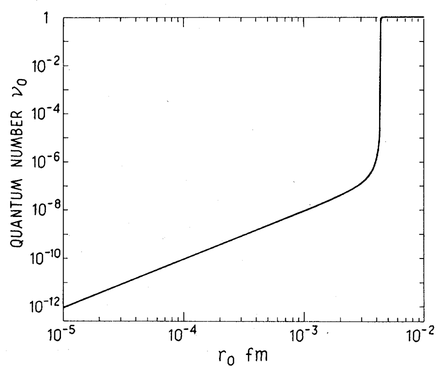

FIG. 3. Quantum number for the hydrogen 1s, $F=0$ state.

It should be remarked that the preceding analysis of limiting behavior for r_0 less than 1 fm has been a purely mathematical exercise. The modified Fermi potential does not, in any sense, represent actual nuclear structure. Nor does it even correctly represent the electron in a region where its behavior must be manifestly relativistic.

IV. PERTURBATION EXPANSION

Since λ_F is a natural scale parameter in the operator $\mathcal{H}'$, expansion of the energy in powers of λ_F will identify terms corresponding to the various orders of perturbation theory. The quantum defect given by (37) can be expanded in powers of λ_F:

$$\delta_{n,F}\approx\lambda_F Z(1-n\rho)-\lambda_F^2 Z^2\left(\frac{1}{n\rho}-\ln\rho-H_n-\frac{n-1}{2n}-\gamma\right)+\cdots, \tag{44}$$

provided that

$$|\lambda_F Z(1/n\rho-\cdots)|<1. \tag{45}$$

Correspondingly, for the energy [cf. (34)],

$$E_{n,F}\approx-\frac{Z^2}{2n^2}+\lambda_F\frac{Z^3}{n^3}(1-n\rho)-\lambda_F^2\frac{Z^4}{n^3}\left(\frac{1}{n\rho}-\ln\rho-H_n+\frac{4-n}{2n}-\gamma\right)+\cdots, \tag{46}$$

up to terms $O(\rho)$ with respect to 1. We therefore identify

$$E_{n,F}^{(1)}\approx\lambda_F(Z^3/n^3)(1-2Zr_0), \tag{47}$$

$$E_{n,F}^{(2)}\approx-\lambda_F^2\frac{Z^4}{n^3}\left[\frac{1}{2Zr_0}-\ln\left(\frac{2Zr_0}{n}\right)-H_n+\frac{4-n}{2n}-\gamma\right]. \tag{48}$$

The first-order energy corresponds to

$$E_{n,F}^{(1)}=\lambda_F\pi|\psi_n(r_0)|^2=\lambda_F\frac{Z^3}{n^3}\left|\frac{M_n(\rho)}{\rho}\right|^2, \tag{49}$$

under the approximation for $\rho \ll 1$,

$$|M(\rho)/\rho|^2\approx 1-n\rho. \tag{50}$$

It should now be apparent why divergences occur in perturbation calculations using the Fermi potential. If the expansion (46) is spuriously applied as $r_0 \to 0$, in violation of condition (45), only the first-order term will approach a finite limit, corresponding to the Fermi formula (2), but second-order and higher perturbation terms will diverge.

The second-order energy (48) can be compared with results obtained by Power and Pitzer[8] (PP) and Gregson, Hall, and Rees[9] (GHR) for $Z=1$, $n=1$ and 2. Expressing the constant term in (48) numerically, we can write

$$E_{1,F}^{(2)}\approx\lambda_F^2\left[-\frac{1}{2r_0}+\ln r_0+\begin{cases}0.7704\\ -0.0665\ (\mathrm{PP})\\ 0.5992\ (\mathrm{GHR})\end{cases}\right],$$

$$8E_{2,F}^{(2)}\approx\lambda_F^2\left[-\frac{1}{2r_0}+\ln r_0+\begin{cases}1.5772\\ 0.7403\ (\mathrm{PP})\\ 1.4061\ (\mathrm{GHR})\end{cases}\right]. \tag{51}$$

Our results agree with those of PP and GHR up to reciprocal and logarithmic terms.[24] The numerical discrepancies in the constant term are rather trivial in any event since r_0 of the order of 1.4 fm ($2.6\times10^{-5}\ a_0$) gives $1/(2r_0)\approx 2\times10^4$ and $\ln r_0\approx 10$. Remarkably, for all three computations,

$$8E_{2,F}^{(2)}-E_{1,F}^{(2)}=(\tfrac{3}{2}-\ln 2)\lambda_F^2=0.8069\lambda_F^2. \tag{52}$$

The last result can be applied to the $1s$-$2s$ hyperfine structure anomaly[8]:

$$\frac{\Delta\nu_{2s}}{\Delta\nu_{1s}}=\frac{1}{8}(1+R),\quad R=(34.6\pm0.3)\times10^{-6}. \tag{53}$$

The calculated residual is $R=\frac{1}{4}(2\ln 2-3)\lambda=-0.08\times10^{-6}$, much smaller than the experimental uncertainty. The residual is, in fact, quite satisfactorily accounted for by relativistic and radiative corrections.[25]

V. EIGENFUNCTIONS

In Sec. II it was deduced that the Schrödinger equation (15) possesses solutions of the form

$$P_\nu(r)=\frac{\lambda_F}{2r_0^2}P_\nu(r_0)g(r,r_0,k),\quad \nu=Z/k. \tag{54}$$

The Coulomb Green's function defined by (17) has the formal structure

$$g(r,r_0,k)=\sum_n\frac{P_n(r)P_n(r_0)}{k^2-k_n^2} \tag{55}$$

in terms of the unperturbed radial functions $P_n(r)=(Z/n)^{1/2}M_n(2Zr/n)$. In view of the nonstandard method by which these solutions were obtained, it would be reassuring to demonstrate their mutual orthogonality. Consider accordingly the overlap integral

$$\int_0^\infty P_\nu(r)P_{\nu'}(r)\,dr=\frac{\lambda_F^2}{4r_0^4}P_\nu(r_0)P_{\nu'}(r_0)\times\int_0^\infty g(r,r_0,k)g(r,r_0,k')\,dr. \tag{56}$$

Making use of (55), we find

$$\begin{aligned}\int_0^\infty g(r,r_0,k)g(r,r_0,k')\,dr&=\sum_n\frac{|P_n(r_0)|^2}{(k^2-k_n^2)(k'^2-k_n^2)}\\&=\frac{1}{k^2-k'^2}\left(\sum_n\frac{|P_n(r_0)|^2}{k'^2-k_n^2}-\sum_n\frac{|P_n(r_0)|^2}{k^2-k_n^2}\right)\\&=(k^2-k'^2)^{-1}[g(r_0,r_0,k')-g(r_0,r_0,k)].\end{aligned} \tag{57}$$

Now, (54) with $r=r_0$ implies that

$$g(r_0,r_0,k)=\mathrm{const}=g(r_0,r_0,k')$$

for every k which corresponds to an eigenvalue of the Schrödinger equation. Therefore (57) vanishes for $k\neq k'$ and there follows the orthogonality condition

$$\int_0^\infty P_\nu(r)P_{\nu'}(r)\,dr=0,\quad \nu\neq\nu'. \tag{58}$$

The eigenfunctions (54) can be normalized by appropriate scaling of the factor $P_\nu(r_0)$. Formally this corresponds to the condition

$$P_\nu(r_0)=\frac{2r_0^2}{\lambda_F}\left(\sum_n\frac{|P_n(r_0)|^2}{(k^2-k_n^2)^2}\right)^{-1/2}. \tag{59}$$

The sum in (59) equals $-\partial g(r_0,r_0,k)/\partial k^2$ but otherwise has no simple analytic representation.

Normalization to $[1+O(\delta)]$ is much simpler and should be quite adequate in most applications. For $r>r_0$ [cf. (25)],

$$P_\nu^{>}(r)=-\frac{\lambda_F}{4kr_0^2}P_\nu(r_0)\Gamma(1-\nu)M_\nu(2kr_0)W_\nu(2kr). \tag{60}$$

The desired normalization can be effected by making the following first-order approximations in (60):

$$P_\nu(r_0) \approx P_n(r_0) = (Z/n)^{1/2} M_n(\rho),$$
$$M_\nu(2kr_0) \approx M_n(\rho), \quad \Gamma(1-\nu) \approx -(-1)^{n-1}/(n-1)!\,\delta,$$
$$\delta \approx \lambda_F Z |M_n(\rho)/\rho|^2, \quad k \approx Z/n. \tag{61}$$

Thus

$$P_\nu^>(r) = [(-1)^{n-1}/n!]\,(Z/n)^{1/2} W_\nu(2kr). \tag{62}$$

The corresponding wave function for $r < r_0$, as determined by the continuity and derivative conditions [cf. (26)], is

$$P_\nu^<(r) = \frac{(-1)^{n-1}}{n!}\left(\frac{Z}{n}\right)^{1/2} \frac{W_\nu(2kr_0)}{M_\nu(2kr_0)} M_\nu(2kr). \tag{63}$$

Note that (62), (63) still represents an exact solution of the Schrödinger equation.

For $2kr \ll 1$, it can be shown that[26]

$$M_\nu(2kr) \sim 2kr, \quad W_\nu(2kr) \sim 1/\Gamma(1-\nu) = O(\delta). \tag{64}$$

It follows that

$$\int_0^{r_0} |P_\nu^<(r)|^2\, dr = O(\delta^2) O(r_0). \tag{65}$$

The analogous integral with $P_\nu^>(r)$ gives a quantity of the same order in δ and r_0. Therefore,

$$\int_0^\infty |P_\nu^>(r)|^2\, dr = 1 + O(\delta), \tag{66}$$

since substitution of $P_\nu^>(r)$ for $P_\nu^<(r)$ between 0 and r_0 introduces an error at most $O(\delta^2)$. Moreover, the integral over the Whittaker function $W_\nu(2kr)$ continues to exist even when the lower limit is thus extended to $r = 0$.

For the 1s state of hydrogen, as shown in Appendix B [Eq. (B23)] for $\nu = 1 + \delta$, $Z = 1$,

$$P_{1s}(r) = W_\nu(2r/\nu)$$
$$\approx 2re^{-r}[1 + \delta(-1/2r + \ln 2r - 1 + r)]. \tag{67}$$

This agrees, within a constant term, with the first-order perturbed wave function for a hydrogen atom in a Fermi potential, as derived by Schwartz.[5] The radial function (67) in the integral (66) gives

$$\int_0^\infty |P_{1s}(r)|^2\, dr = 1 + (3 - 2\gamma)\delta + O(\delta^2), \tag{68}$$

with use of the definite integral

$$\int_0^\infty x^2 e^{-x} \ln x\, dx = 3 - 2\gamma. \tag{69}$$

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APPENDIX A: DERIVATION OF THE S-WAVE COULOMB GREEN'S FUNCTION

The Green's function for a Sturm-Liouville differential operator satisfies

$$\left(\frac{\partial}{\partial x} p(x) \frac{\partial}{\partial x} - q(x)\right) g(x, x') = \delta(x - x'). \tag{A1}$$

If $u_0(x)$ represents a solution of the homogeneous equation satisfying specified boundary conditions at $x = 0$ and $u_\infty(x)$ designates the corresponding solution for $x \to \infty$, then[27]

$$g(x, x') = -\frac{u_0(x_<) u_\infty(x_>)}{p(x) \mathcal{W}\{u_\infty, u_0\}},$$
$$\mathcal{W}\{u_\infty, u_0\} \equiv u_\infty(x) u_0'(x) - u_\infty'(x) u_0(x). \tag{A2}$$

To apply this prescription to Eq. (17), note that the solution fulfilling conditions (18) at $r = 0$ is the Whittaker function $M_{i\nu}(-2ikr)$. The solution fulfilling (19) as $r \to \infty$ is $W_{i\nu}(-2ikr)$, provided that $\operatorname{Im} k > 0$. The Wronskian for the two functions is[28]

$$\mathcal{W}\{W_{i\nu}(z), M_{i\nu}(z)\} = 1/\Gamma(1 - i\nu) \tag{A3}$$

or, with respect to the variable r,

$$\mathcal{W}\{W_{i\nu}(-2ikr), M_{i\nu}(-2ikr)\} = -2ik/\Gamma(1 - i\nu). \tag{A4}$$

For Eq. (17), $p(r) = 1$. It follows therefore that

$$g(r, r_0, k) = (2ik)^{-1} \Gamma(1 - i\nu) M_{i\nu}(-2ikr_<)$$
$$\times W_{i\nu}(-2ikr_>). \tag{A5}$$

APPENDIX B: WHITTAKER FUNCTIONS FOR SMALL QUANTUM DEFECT

Solutions of the Schrödinger equation for a Coulomb system perturbed by a modified Fermi potential involve the Whittaker functions $M_\nu(2Zr/\nu)$ and $W_\nu(2Zr/\nu)$ with $\nu = n + \delta$, $n = 1, 2, \ldots$, $\delta \sim 10^{-7}$. These differ only minutely from the corresponding functions of integral index, which pertain to the unperturbed Coulomb problem. Direct computational use of M_ν and W_ν would require at least eight significant-figure accuracy in order to take adequate account of the perturbation. It is clearly more efficient to make these deviations explicit by expanding the Whittaker functions to first order in the quantum defect. Thus we write

$$M_\nu\left(\frac{2Zr}{\nu}\right) \approx M_n\left(\frac{2Zr}{n}\right) + \delta \frac{\partial}{\partial \nu} M_\nu\left(\frac{2Zr}{\nu}\right)\Big|_{\nu=n}, \tag{B1}$$

and analogously for W. The main task is to evaluate the derivatives of the Whittaker functions with respect to ν.

The function $M_\nu(z)$ is defined in terms of the confluent hypergeometric function[29]:

$$M_\nu(z) \equiv z e^{-z/2} {}_1F_1(1-\nu; 2; z),$$

$${}_1F_1(1-\nu; 2; z) = \sum_{k=0}^{\infty} \frac{(1-\nu)_k}{(2)_k k!} z^k,$$

$$(\alpha)_k \equiv \alpha(\alpha+1)\cdots(\alpha+k-1) = \Gamma(\alpha+k)/\Gamma(\alpha) \qquad \text{(B2)}$$

The quantum number ν occurs in both the index and the argument of the function. The required first derivative is thus a sum of two parts:

$$\left.\frac{\partial M_\nu(z)}{\partial \nu}\right|_{\nu=n} = \left.\frac{\partial M_\nu(\rho)}{\partial \nu}\right|_{\nu=n} - \frac{\rho}{n} \left.\frac{\partial M_n(z)}{\partial z}\right|_{z=\rho},$$

$$z \equiv 2Zr/\nu, \quad \rho \equiv 2Zr/n. \qquad \text{(B3)}$$

The derivative with respect to argument is easy in view of the identity[30]

$$\frac{\partial}{\partial z} {}_1F_1(1-n; 2; z) = \tfrac{1}{2}(1-n) {}_1F_1(2-n; 3; z). \qquad \text{(B4)}$$

In full,

$$\left.\frac{\partial M_n(z)}{\partial z}\right|_{z=\rho} = \rho e^{-\rho/2}\left[\left(\frac{1}{\rho} - \frac{1}{2}\right) {}_1F_1(1-n; 2; \rho) + \tfrac{1}{2}(1-n) {}_1F_1(2-n; 3; \rho)\right]. \qquad \text{(B5)}$$

The derivative with respect to the index follows from the relation

$$\frac{\partial}{\partial \nu}(1-\nu)_k = -(1-\nu)_k H_k(1-\nu),$$

$$H_k(\alpha) \equiv \frac{1}{\alpha} + \frac{1}{\alpha+1} + \cdots + \frac{1}{\alpha+k-1}, \quad H_k(1) = H_k. \qquad \text{(B6)}$$

Now

$$\left.\frac{\partial}{\partial \nu}(1-\nu)_k\right|_{\nu=n} = \begin{cases} -(1-n)_k H_k(1-n) & \text{for } k \leqslant n-1 \\ (-1)^n (n-1)!\,(k-n)! & \text{for } k \geqslant n, \end{cases} \qquad \text{(B7)}$$

and therefore,

$$\left.\frac{\partial}{\partial \nu} {}_1F_1(1-\nu; 2; \rho)\right|_{\nu=n} = -\sum_{k=1}^{n-1} \frac{(1-n)_k}{(2)_k k!} H_k(1-n)\rho^k + (-1)^n (n-1)! \sum_{k=n}^{\infty} \frac{(k-n)!}{(2)_k k!}\rho^k. \qquad \text{(B8)}$$

Using (B2), (B3), (B5), and (B8) in (B1) we obtain the desired first-order result:

$$M_\nu(z) \approx M_n(\rho) + \delta\rho e^{-\rho/2}\left[\left(\frac{\rho}{2n} - \frac{1}{n}\right) {}_1F_1(1-n; 2; \rho) + \frac{n-1}{2n}\rho\, {}_1F_1(2-n; 3; \rho) - \sum_{k=1}^{n-1} \frac{(1-n)_k}{(2)_k k!} H_k(1-n)\rho^k + (-1)^n (n-1)! \sum_{k=n}^{\infty} \frac{(k-n)!}{(2)_k k!}\rho^k\right]. \qquad \text{(B9)}$$

Specifically, for the 1*s* state ($n=1$, $\nu=1+\delta$),

$$M_{1+\delta}(z) \approx \rho e^{-\rho/2}\{1 + \delta[-1 + \tfrac{1}{2}\rho - f(\rho)]\}, \qquad \text{(B10)}$$

where

$$f(\rho) \equiv \sum_{k=1}^{\infty} \frac{(k-1)!}{(k+1)!\,k!}\rho^k = \int_0^\rho \frac{e^x - 1 - x}{x^2}\, dx. \qquad \text{(B11)}$$

This latter function was encountered also by Hameka[31] and Hostler[32] in connection with the reduced Coulomb Green's function. Integration by parts gives

$$f(\rho) = -\left(\frac{e^\rho - 1 - \rho}{\rho}\right) + \int_0^\rho \frac{e^x - 1}{x}\, dx, \qquad \text{(B12)}$$

and[33]

$$\int_0^\rho \frac{e^x - 1}{x}\, dx = \mathrm{Ei}(\rho) - \ln\rho - \gamma. \qquad \text{(B13)}$$

The analogous computation for $W_\nu(z)$ is most readily approached using the asymptotic series[34]

$$W_\nu(z) \sim z^\nu e^{-z/2} {}_2F_0(1-\nu, -\nu;; -1/z),$$

$${}_2F_0(1-\nu, -\nu;; -1/z) = \sum_{k=0}^{\infty} \frac{(1-\nu)_k(-\nu)_k}{k!\,(-z)^k}. \qquad \text{(B14)}$$

Again

$$\left.\frac{\partial W_\nu(z)}{\partial \nu}\right|_{\nu=n} = \left.\frac{\partial W_\nu(\rho)}{\partial \nu}\right|_{\nu=n} - \frac{\rho}{n} \left.\frac{\partial W_n(z)}{\partial z}\right|_{z=\rho}. \qquad \text{(B15)}$$

For $\nu=n$, the divergent series (B14) reduces to a polynomial since

$${}_2F_0(1-n, -n;; -1/z) = \sum_{k=0}^{n-1} \frac{(1-n)_k(-n)_k}{k!\,(-z)^k}. \qquad \text{(B16)}$$

By use of the identities

$$(1-n)_k = (-1)^k (n-1)!/(n-k-1)!,$$

$$(-n)_k = (-1)^k n!/(n-k)!, \qquad \text{(B17)}$$

we find

$$W_n(z) = (-1)^{n-1} n!\, z e^{-z/2} \sum_{k=0}^{n-1} \frac{(1-n)_k}{(2)_k k!} z^k = (-1)^{n-1} n!\, M_n(z). \qquad \text{(B18)}$$

The derivative with respect to the argument thus follows from (B5). For the derivative with respect to the index, we require analogs of (B6) and (B7), viz.,

$$\frac{\partial}{\partial \nu}(1-\nu)_k(-\nu)_k = -(1-\nu)_k(-\nu)_k[H_k(1-\nu)+H_k(-\nu)]$$

$$\frac{\partial}{\partial \nu}(1-\nu)_k(-\nu)_k\bigg|_{\nu=n} = \begin{cases} -(1-n)_k(-n)_k\,[H_k(1-n)+H_k(-n)]\,, \text{ for } k\leqslant n-1 \\ n!\,(n-1)!\,, \quad \text{for } k=n, \\ 0, \text{ for } k>n \end{cases} \tag{B19}$$

The divergent series again terminates, for

$$\frac{\partial}{\partial \nu}\,{}_2F_0(1-\nu,-\nu;;-1/\rho)\bigg|_{\nu=n} = -\sum_{k=1}^{n-1}\frac{(1-n)_k(-n)_k}{k!\,(-\rho)^k}[H_k(1-n)+H_k(-n)] + \frac{(-1)^n(n-1)!}{\rho^n}$$

$$= (-1)^n n!\left(\sum_{k=0}^{n-2}\frac{(1-n)_k}{(2)_k k!}[H_{n-k-1}(1-n)+H_{n-k-1}(-n)]\rho^k + \frac{1}{n\rho}\right). \tag{B20}$$

The factor ρ^ν in (B14) contributes a logarithmic term

$$\frac{\partial \rho^\nu}{\partial \nu}\bigg|_{\nu=n} = \rho^n \ln\rho\,. \tag{B21}$$

With (B18), (B5), (B20), and (B21) in (B15) we obtain finally

$$\frac{W_\nu(z)}{(-1)^{n-1}n!} \approx M_n(\rho) + \delta\rho e^{-\rho/2}\left\{\left(-\frac{1}{n}+\frac{\rho}{2n}+\ln\rho\right){}_1F_1(1-n;2;\rho) + \frac{n-1}{2n}\rho\,{}_1F_1(2-n;3;\rho) - \frac{1}{n\rho}\right.$$

$$\left. -\sum_{k=0}^{n-2}\frac{(1-n)_k}{(2)_k k!}[H_{n-k-1}(1-n)+H_{n-k-1}(-n)]\rho^k\right\}. \tag{B22}$$

For the 1*s* state

$$W_{1+\delta}(z) \approx \rho e^{-\rho/2}[1+\delta(-1+\rho/2+\ln\rho-1/\rho)]. \tag{B23}$$

APPENDIX C: ALTERNATIVE DERIVATION OF THE QUANTUM DEFECT FORMULA

For small values of $\rho \equiv 2Zr_0/n$, as well as small δ, Eqs. (B9) and (B22) reduce as follows:

$$\frac{M_\nu(z)}{z} \approx \frac{M_n(\rho)}{\rho}\left[1-\delta\left(\frac{\rho^2}{12n}\right)\right], \tag{C1}$$

$$\frac{W_\nu(z)}{z} \approx (-1)^{n-1}n!\,\frac{M_n(\rho)}{\rho}$$

$$\times\left[1+\delta\left(-\frac{1}{n\rho}+\ln\rho+2H_n-\frac{3n+1}{2n}\right)\right]. \tag{C2}$$

Also

$$M_n(\rho)/\rho \approx 1-\tfrac{1}{2}n\rho \tag{C3}$$

For $\nu=n+\delta$, the Γ function can be approximated with

$$\Gamma(-\nu) = \frac{(-1)^{n-1}}{n!}\left(\frac{1}{\delta}+\gamma-H_n\right)+O(\delta). \tag{C4}$$

Putting (C1)–(C4) into the eigenvalue condition (28), we obtain

$$1 \approx \lambda_F Z\left(\frac{1}{\delta}-\frac{1}{n\rho}+\ln\rho+H_n-\frac{n+1}{2n}+\gamma\right), \tag{C5}$$

apart from terms O(δ), O(ρ), etc. Solving for δ then gives Eq. (37).

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