New techniques for evaluating parity-conserving and parity-violating contact interactions

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The accurate evaluation of expectation values such as $I_1 = \langle\psi|\delta(\vec{r}_1)|\psi\rangle$ and $I_{12} = \langle\psi|\delta(\vec{r}_1-\vec{r}_2)|\psi\rangle$, where $\psi = \psi(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)$ is an eigenfunction of a Hamiltonian H is of interest for a variety of problems in atomic physics. Transformations are found to new forms I_1' and I_{12}', which are likely to give considerably more accurate values when, as is usually the case, only approximate wave functions are available. A successful test of the method is presented for the case of electron-electron and electron-nucleus contact interactions in helium. We give some identities which may be similarly useful in the evaluation of off-diagonal matrix elements of relativistic operators such as $\gamma_5\delta(\vec{r}_1)$, which arise from the parity-violating part of the neutral-current interaction and are important in the calculation of parity mixing in atoms.

I. INTRODUCTION

There are a number of situations in which it is necessary to evaluate matrix elements of an electron-nucleon or an electron-electron operator involving a δ function of the separation $\vec{r}$ between the two particles. A list of examples would include hyperfine interactions, relativistic spin-spin interactions and neutral current, parity nonconserving interactions between electrons and nucleons or between two electrons.[1] In each case one has only approximate wave functions for the electrons, and it is not clear *a priori* to what extent these wave functions give accurate values for the matrix elements of δ-function operators.

In this paper we present some identities that can be used to transform the matrix elements of the indicated type into other forms that involve the electron wave functions over the full range of interparticle separations. Since the usual approaches do not generate wave functions that are especially accurate at small separations, we expect that the transformed matrix elements will be more accurately approximated by the available wave functions than the original ones would be. To be concrete, let us consider two particles 1 and 2 in an external field, with a wave function $\psi = \psi(\vec{r}_1,\vec{r}_2)$ which satisfies

$$H\psi = E\psi\,, \quad H = \vec{p}_1^{\,2}/2m_1 + \vec{p}_2^{\,2}/2m_2 + V^{\rm tot}, \tag{1.1}$$

where $V^{\rm tot} = V_1^{\rm ex} + V_2^{\rm ex} + V_{12}$, with $V_i^{\rm ex}$ the interaction of i with the external field and V_{12} the mutual interaction of 1 and 2. The identity in question for $\delta(\vec{r}_1)$ then takes the form

$$\langle\psi\,|\,\delta(\vec{r}_1)\,|\,\psi\rangle = \langle\psi\,|\,D_1\,|\,\psi\rangle\,, \tag{1.2}$$

where, with $V^{\rm tot}$ assumed to be local,

$$D_1 = \frac{m_1}{2\pi}\frac{\partial V^{\rm tot}}{\partial r_1} - \frac{1}{2\pi}r_1^{-3}\vec{l}_1^{\,2} \tag{1.3}$$

with $r_1 = |\vec{r}_1|$ and $\vec{l}_1 = \vec{r}_1\times\vec{p}_1$. The identity for $\delta(\vec{r}) = \delta(\vec{r}_1 - \vec{r}_2)$ reads

$$\langle\psi\,|\,\delta(\vec{r})\,|\,\psi\rangle = \langle\psi\,|\,D_{12}\,|\,\psi\rangle\,, \tag{1.4}$$

where

$$D_{12} = \frac{\mu}{2\pi}\frac{\partial V^{\rm tot}}{\partial r} - \frac{1}{2\pi}r^{-3}\vec{l}^{\,2}\,. \tag{1.5}$$

Here $\mu = m_1m_2/(m_1+m_2)$ is the reduced mass and $\vec{l} = \vec{r}\times\vec{p}$ is the relative orbital angular momentum, with $\vec{p} = i^{-1}\partial/\partial\vec{r}$ the momentum conjugate to the relative coordinate $\vec{r}$.

To test our expectation we have evaluated $\langle\delta(\vec{r}_1)\rangle$ and $\langle D_1\rangle$ as well as $\langle\delta(\vec{r})\rangle$ and $\langle D_{12}\rangle$ using various Hylleraas wave functions for helium. We indeed find that the D form of the matrix element agrees with the exact value much more closely than does the δ form when both are evaluated with the same approximate wave function. In particular, the evaluation of D_{12} with a three-parameter wave function gives a value whose error is only 0.6%, compared to the $\delta(\vec{r})$ form for which the error is 8.6% — a gain in accuracy of *more than an order of magnitude*.

In the absence of an external field and with V_{12} a local potential, e.g., $V_{12} = V(r)$, (1.4) reduces to

$$\langle\phi\,|\,\delta(\vec{r})\,|\,\phi\rangle = (\mu/2\pi)\langle\phi\,|\,V'(r)\,|\,\phi\rangle - (1/2\pi)\langle\phi\,|\,r^{-3}\vec{l}^{\,2}\,|\,\phi\rangle\,, \tag{1.6}$$

where $\phi = \phi(\vec{r})$ is a bound-state eigenfunction of $\vec{p}^{\,2}/2\mu + V(r)$. For an S state the $\vec{l}^{\,2}$ term vanishes and (1.6) reduces to

$$|\,\phi(0)\,|^2 = (\mu/2\pi)\langle\phi\,|\,V'(r)\,|\,\phi\rangle\,, \tag{1.7}$$

a formula which has become familiar in recent years from its application to the naive charmonium model; with $V = ar + b$ the right-hand side of (1.7)

is just $\mu a/2\pi$, independent of the radial quantum number n.[2] However, for a state with $l \neq 0$, the δ-function term vanishes and one gets instead a relation between the mean value of r^{-3} and $V'(r)$:

$$\langle r^{-3}\rangle = [\mu/l(l+1)]\langle V'(r)\rangle . \tag{1.8}$$

For a linear potential this implies that $\langle r^{-3}\rangle$ is independent of n. This observation may be of interest for the fine structure since the short-range spin-dependent interactions coming from exchange of a massless vector quantum have an r^{-3} spatial dependence. For the popular choice $V = ar + b - \lambda/r$ (1.8) relates $\langle r^{-3}\rangle$ to $\langle r^{-2}\rangle$.

The derivation of the identities (1.2) and (1.4) is given in Sec. II, together with similar identities which hold for a system of more than two particles. The application of (1.2) and (1.4) to electron-electron and electron-nucleon contact interactions in the helium atom is given in Sec. III. In Sec. IV these ideas are extended to relativistic systems and to off-diagonal matrix elements of operators of the type $\mathcal{O}\,\delta(\vec{r}_1)$ or $\mathcal{O}\,\delta(\vec{r}_{12})$ where $\mathcal{O}$ is a Dirac matrix. The resulting identities are of a type which may be useful in the evaluation of parity-violating effects in atomic physics. Section V contains a summary of our results and a simple physical interpretation of identity (1.6). In Appendix A we describe some details of the evaluation of $\langle D_1\rangle$ and $\langle D_{12}\rangle$ for helium. In Appendix B we explain how rigorous estimates of the accuracy of $\langle\delta(\vec{r}_1)\rangle$ and $\langle\delta(\vec{r}_{12})\rangle$ can be made when these quantities are evaluated with approximate wave functions.

II. δ-FUNCTION IDENTITIES FOR N-PARTICLE SYSTEMS

A. $\delta(\vec{r}_1)$-type identity

Consider first a single particle 1 in an external field, described by a Hermitian Hamiltonian H_1,

$$H_1 = K_1 + V_1^{\rm ex}, \quad K_1 = \vec{p}_1^{\,2}/2m_1 \tag{2.1}$$

and wave function $\psi = \psi(\vec{r}_1)$ satisfying

$$(H_1 - E)\psi = 0 . \tag{2.2}$$

Let $\partial/\partial r_1$ denote the derivative with respect to $r_1 = |\vec{r}_1|$ with $\hat{r}_1 = \vec{r}_1/r_1$ fixed. Using polar coordinates for the Laplacian $\vec{\nabla}_1^2$ one finds

$$\left[\frac{\partial}{\partial r_1}, K_1\right] = (m_1 r_1^2)^{-1}\frac{\partial}{\partial r_1} - (m_1 r_1^3)^{-1}\vec{l}_1^{\,2}, \tag{2.3}$$

where $\vec{l}_1 = \vec{r}_1 \times \vec{p}_1$. It follows that

$$\left[\frac{\partial}{\partial r_1}, H_1\right] = (m_1 r_1^2)^{-1}\frac{\partial}{\partial r_1} - (m_1 r_1^3)^{-1}\vec{l}_1^{\,2} + \left[\frac{\partial}{\partial r_1}, V_1^{\rm ex}\right]. \tag{2.4}$$

For simplicity, we assume that the interaction $V_1^{\rm ex}$ with the external field is local, $V_1^{\rm ex} = V_1^{\rm ex}(\vec{r}_1)$ only. Then the commutator term in (2.4) is just $\partial V_1/\partial r_1$. On taking the expectation value of (2.4) with a solution ψ of (2.2) we get

$$0 = m_1^{-1}\langle\psi\,|\,r_1^{-2}\frac{\partial}{\partial r_1}\,|\,\psi\rangle + \langle\psi|\frac{\partial V_1^{\rm ex}}{\partial r_1} - (m_1 r_1^3)^{-1}\vec{l}_1^{\,2}|\,\psi\rangle . \tag{2.5}$$

Here we have assumed that ψ vanishes sufficiently rapidly as $r_1 \to \infty$ so that $\langle\psi|H_1\partial/\partial r_1|\psi\rangle = \langle H_1\psi|\partial/\partial r_1|\psi\rangle$, which is certainly the case when ψ is a bound state. If we add the complex conjugate of (2.5) to Eq. (2.5) we get

$$-\left[\langle\psi|\,r_1^{-2}\frac{\partial}{\partial r_1}\,|\,\psi\rangle + \text{c.c.}\right] = 2\langle\psi|\,m_1\frac{\partial V_1^{\rm ex}}{\partial r_1} - r_1^{-3}\vec{l}_1^{\,2}|\psi\rangle . \tag{2.6}$$

The left-hand side of (2.6) is just

$$-\int d\Omega_1\int_0^\infty dr_1\,\frac{\partial}{\partial r_1}(\psi^*\psi) = 4\pi\,|\,\psi(\vec{r}_1 = 0)\,|^2 \tag{2.7}$$

provided that ψ vanishes at $r_1 = \infty$. It follows that for a bound state and with $V_1^{\rm ex}$ Hermitian, (2.6) may be written as

$$\langle\psi|\,\delta(\vec{r}_1)\,|\,\psi\rangle = \langle\psi|\,D_1\,|\,\psi\rangle , \tag{2.8}$$

with D_1 given by

$$D_1 = \frac{m_1}{2\pi}\frac{\partial V_1^{\rm ex}}{\partial r_1} - \frac{1}{2\pi}r_1^{-3}\vec{l}_1^{\,2} . \tag{2.9}$$

The identity (2.8) is a special case of (1.2). The generalization of (2.8) to a bound state of N particles in an external field is immediate, because the total kinetic energy is a sum of one-particle operators. Thus with

$$H = \sum_{j=1}^{N} K_j + V^{\rm tot}; \quad K_j = \vec{p}_j^{\,2}/2m_j , \tag{2.10}$$

and a wave function $\psi = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ satisfying

$$(H - E)\psi = 0 \tag{2.11}$$

the analog of (2.4) is simply

$$\left[\frac{\partial}{\partial r_1}, H\right] = (m_1 r_1^2)^{-1}\frac{\partial}{\partial r_1} - (m_1 r_1^3)^{-1}\vec{l}_1^{\,2} + \left[\frac{\partial}{\partial r_1}, V^{\rm tot}\right]. \tag{2.12}$$

On taking the expectation value of (2.12) with ψ and proceeding as in the one-particle case, we then get the sought after identity:

$$I_1 = I_1' , \tag{2.13}$$

where

$$I_1 \equiv \langle\psi|\,\delta(\vec{r}_1)\,|\,\psi\rangle , \quad I_1' \equiv \langle\psi|\,D_1^{\rm tot}|\,\psi\rangle \tag{2.14}$$

with

$$D_1^{\rm tot} = \frac{m_1}{2\pi}\frac{\partial V^{\rm tot}}{\partial r_1} - \frac{1}{2\pi}r_1^{-3}\vec{l}_1^{\,2} . \tag{2.15}$$

Again we have assumed that $V^{\rm tot}$ is Hermitian and local. If $V^{\rm tot}$ is not local, the replacement

$$\frac{\partial V^{\rm tot}}{\partial r_1} \to \frac{1}{2}\left(\left[\frac{\partial}{\partial r_1}, V^{\rm tot}\right] + \text{h.c.}\right) \tag{2.16}$$

should be made in the definition (2.15). For $N=2$, the identity (2.13) coincides with (1.2).

B. $\delta(\vec{r}_{12})$-type identity

The derivation of an identity such as (1.4) is based not only on the additivity of the kinetic energy but on the separability of K_1+K_2 into a "relative" and "total" kinetic energy. Thus with

$$\vec{r}=\vec{r}_1-\vec{r}_2\,, \quad \vec{R}=(m_1\vec{r}_1+m_2\vec{r}_2)/(m_1+m_2) \tag{2.17}$$

and

$$\vec{p}=\frac{1}{i}\frac{\partial}{\partial \vec{r}}\,, \quad \vec{P}=\frac{1}{i}\frac{\partial}{\partial \vec{R}} \tag{2.18}$$

we have

$$K_1+K_2=\vec{p}^2/2\mu+\vec{P}^2/2(m_1+m_2)\,, \tag{2.19}$$

where

$$\mu=(m_1m_2)/(m_1+m_2) \tag{2.20}$$

is the reduced mass. Let $\partial/\partial r$ denote differentiation with respect to $r=|\vec{r}|$, with $\hat{r}$ and $\vec{R}$ held fixed. Then for a Hamiltonian of the form (2.10) we get, using (2.19),

$$\left[\frac{\partial}{\partial r}, H-E\right]=(\mu r^2)^{-1}\frac{\partial}{\partial r}-(\mu r^3)^{-1}\vec{l}^2+\left[\frac{\partial}{\partial r}, V^{\rm tot}\right], \tag{2.21}$$

where $\vec{l}=\vec{r}\times\vec{p}$ is the relative orbital angular momentum of 1 and 2. We now take the expectation value of (2.21) with a bound-state wave function $\psi=\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ and write the part $d\tau_{12}=d\vec{r}_1\,d\vec{r}_2$ of the volume element $d\tau$ in the form $d\tau_{12}=d\vec{r}\,d\vec{R}$ and proceed as before. The result is

$$I_{12}=I'_{12}\,, \tag{2.22}$$

where

$$I_{12}\equiv\langle\psi|\,\delta(\vec{r})\,|\psi\rangle\,, \quad I'_{12}\equiv\langle\psi|\,D^{\rm tot}_{12}|\psi\rangle \tag{2.23}$$

and

$$D^{\rm tot}_{12}=\frac{\mu}{2\pi}\frac{\partial V^{\rm tot}}{\partial r}-\frac{1}{2\pi}r^{-3}\vec{l}^2\,. \tag{2.24}$$

Again if $V^{\rm tot}$ is not local, the replacement analogous to (2.16) should be made for $\partial V^{\rm tot}/\partial r$. For $N=2$, the identity (2.22) coincides with (1.4).

III. APPLICATION TO ATOMS

A. Simplifications

For the case of an N-electron atom or ion, $V^{\rm tot}$ is a sum of one- and two-body operators,

$$V^{\rm tot}=\sum_{i=j}^{N}V_{\rm ex}(r_i)+\sum_{i<j}V_{e\text{-}e}(r_{ij})\,, \tag{3.1}$$

where $V_{\rm ex}$ is the electron-nucleus interaction and $V_{e\text{-}e}$ the electron-electron interaction. Moreover, the many-body wave function $\Psi=\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ (spin coordinates are suppressed) satisfies the antisymmetry principle. The potential terms entering the identities (2.13) and (2.22) can then be made more explicit. From (3.1) we have

$$\frac{\partial V^{\rm tot}}{\partial r_1}=V'_{\rm ex}(r_1)+\sum_{j=2}^{N}V'_{e\text{-}e}(r_{1j})\frac{\partial r_{1j}}{\partial r_1} \tag{3.2}$$

and, with $r\equiv r_{12}$,

$$\frac{\partial V^{\rm tot}}{\partial r}=V'_{\rm ex}(r_1)\frac{\partial r_1}{\partial r}+V'_{\rm ex}(r_2)\frac{\partial r_2}{\partial r}+V'_{e\text{-}e}(r)+\sum_{j=3}^{N}\left(V'(r_{1j})\frac{\partial r_{1j}}{\partial r}+V'(r_{2j})\frac{\partial r_{2j}}{\partial r}\right), \tag{3.3}$$

where the primes denote a derivative with respect to the displayed variable. Because of the antisymmetry of Ψ all terms in the sums on j make the same contribution to expectation values, so that

$$\langle\Psi|\frac{\partial V^{\rm tot}}{\partial r_1}|\Psi\rangle=\langle\Psi|\,V'_{\rm ex}(r_1)+(N-1)V'_{e\text{-}e}(r)\frac{\partial r}{\partial r_1}|\Psi\rangle \tag{3.4}$$

and

$$\langle\Psi|\frac{\partial V^{\rm tot}}{\partial r}|\Psi\rangle=\langle\Psi|\,V'_{e\text{-}e}(r)+V'_{\rm ex}(r_1)\frac{\partial r_1}{\partial r}+V'_{\rm ex}(r_2)\frac{\partial r_2}{\partial r}|\Psi\rangle + (N-2)\langle\Psi|\,V'_{e\text{-}e}(r_{13})\frac{\partial r_{13}}{\partial r} + V'_{e\text{-}e}(r_{23})\frac{\partial r_{23}}{\partial r}|\Psi\rangle\,. \tag{3.5}$$

Of course, the contributions of the second and third term in (3.5) are equal as are those of the fourth and fifth terms, but it is convenient to keep the symmetry between 1 and 2 manifest. The partial derivatives entering (3.4) and (3.5) are readily calculated:

$$\frac{\partial r}{\partial r_1}=\frac{r_1^2-r_2^2+r^2}{2r_1r}\,, \quad \frac{\partial r_1}{\partial r}=\frac{r_1^2-r_2^2+r^2}{4r_1r} \tag{3.6}$$

and

$$\frac{\partial r_{13}}{\partial r}=\frac{r_{12}^2+r_{13}^2-r_{23}^2}{4r_{12}r_{13}}\,, \tag{3.7}$$

with $1\leftrightarrow 2$ for $\partial r_2/\partial r$ and $\partial r_{23}/\partial r$.

In practice, for an atom with nuclear charge Ze one has of course

$$V_{\rm ex}(r_i)=-Z\alpha/r_i\,, \quad V_{e\text{-}e}(r)=\alpha/r \tag{3.8}$$

and $V'_{\rm ex}(r_i)=Z\alpha/r_i^2$, $V'_{e\text{-}e}(r)=-\alpha/r^2$. However, the formulas as written in (3.4) and (3.5) remain

valid if the usual local spin-spin interactions and even if spin-orbit interactions are included in H since, e.g.,

$$\left[\frac{\partial}{\partial r_1}, \xi(r_1)\vec{\sigma}_1 \cdot \vec{l}_1\right] = \xi'(r_1)\vec{\sigma}_1 \cdot \vec{l}_1$$

is Hermitian if ξ is real.

B. Contact interactions in helium

For a two-electron atom or ion the Hamiltonian is

$$H = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{\alpha Z}{r_1} - \frac{\alpha Z}{r_2} + \frac{\alpha}{r} . \tag{3.9}$$

The ground-state wave function has the form $\Psi = \psi_0(\vec{r}_1, \vec{r}_2)\chi$, where χ is a Pauli spin-wave function and ψ_0 is the $L=0$ eigenstate of (3.9) with lowest eigenvalue E_0,

$$H\psi_0 = E_0\psi_0 . \tag{3.10}$$

Then the quantities of interest are

$$I_1 = \langle\psi_0|\,\delta(\vec{r}_1)\,|\psi_0\rangle , \quad I_{12} = \langle\psi_0|\,\delta(\vec{r})\,|\psi_0\rangle , \tag{3.11}$$

Using the expressions (2.14) and (2.23) for the transformed quantities I_1' and I_{12}' as well as the relations (3.4) and (3.5), specialized to the case $N=2$ and a Hamiltonian of the form (3.9), we get

$$I_1' = \langle\psi_0|\,D_1\,|\psi_0\rangle , \quad I_{12}' = \langle\psi_0|\,D_{12}\,|\psi_0\rangle , \tag{3.12}$$

where

$$D_1 = \frac{m}{2\pi}\left(\frac{\alpha Z}{r_1^2} - \frac{\alpha}{r^2}\frac{\partial r}{\partial r_1}\right) - \frac{1}{2\pi} r_1^{-3}\vec{l}_1^2 \tag{3.13}$$

and

$$D_{12} = \frac{m}{4\pi}\left(\frac{\alpha Z}{r_1^2}\frac{\partial r_1}{\partial r} + \frac{\alpha Z}{r_2^2}\frac{\partial r_2}{\partial r} - \frac{\alpha}{r^2}\right) - \frac{1}{2\pi} r^{-3}\vec{l}^2 . \tag{3.14}$$

Let $\tilde{\psi}$ denote an approximate rather than an exact solution of (3.9) and define

$$\tilde{I}_1 = \langle\tilde{\psi}|\delta(\vec{r}_1)|\tilde{\psi}\rangle , \quad \tilde{I}_1' = \langle\tilde{\psi}|D_1|\tilde{\psi}\rangle ; \tag{3.15}$$

$$\tilde{I}_{12} = \langle\tilde{\psi}|\,\delta(\vec{r})\,|\tilde{\psi}\rangle , \quad \tilde{I}_{12}' = \langle\tilde{\psi}|D_{12}|\tilde{\psi}\rangle . \tag{3.16}$$

According to what has been suggested above, the quantity $\tilde{I}_1'$ is likely to be closer to the exact value I_1 than $\tilde{I}_1$ and similarly for $\tilde{I}_{12}'$ relative to $\tilde{I}_{12}$. We now test this idea for the case of the helium atom.

Although the nonrelativistic ground-state wave function ψ_0 of He is not known in closed form, numerical work on ψ_0 has reached a high degree of precision. Thus the 1078-parameter wave function of Pekeris[3] gives, in atomic units,

$$I_1 = 1.810\,419 , \quad I_{12} = 0.106\,355 . \tag{3.17}$$

Also important for our purpose is the fact that the degree of exactness of these numbers can be rigorously established, by using techniques such as those developed by Rédei.[4] In particular, as shown in Appendix B, the above values for I_1 and I_{12} differ from the exact values by less than 0.07% and 0.24%, respectively, which is exact enough for making comparisons.

In Tables I(a) and I(b) we show the values of $\tilde{I}_1$ and $\tilde{I}_1'$ and $\tilde{I}_{12}$ and $\tilde{I}_{12}'$, respectively, as computed from the one- and three-parameter Hylleraas-type wave functions $\tilde{\psi} = \tilde{\psi}(s,u,t)$ given by Bethe and Salpeter,[5] who also list values $\tilde{I}_1$ and $\tilde{I}_{12}$ obtained from such wave functions. The values of $\tilde{I}_1'$ and $\tilde{I}_{12}'$ were computed from (3.15) and (3.16) with the D's defined by (3.13) and (3.14); the integrals encountered (see Appendix A) can all be done analytically. As can be seen, there is a striking gain in accuracy in going from $\tilde{I}$ to $\tilde{I}'$, both for $\delta(\vec{r}_1)$ and for $\delta(\vec{r}_{12})$. In particular, with only three parameters, use of I_1' and I_{12}' gives *results which are within a few tenths of a percent of the exact*

TABLE I. (a) Comparison of $\tilde{I}_1 = \langle\tilde{\psi}\,|\delta(\vec{r}_1)|\,\tilde{\psi}\rangle$ and $\tilde{I}_1' = \langle\tilde{\psi}|D_1|\tilde{\psi}\rangle$ for one- and three-parameter Hylleraas-type wave functions $\tilde{\psi}$ for the ground state of He; D_1 is given by Eq. (3.13) of the text. The column labeled "error" shows the percentage difference from the exact value $I_1 = \langle\psi_0|\delta(\vec{r}_1)|\psi_0\rangle = \langle\psi_0|D_1|\psi_0\rangle = 1.8104$ a.u. (b) Similar comparison of $\tilde{I}_{12} = \langle\tilde{\psi}|\delta(\vec{r})|\tilde{\psi}\rangle$ and $\tilde{I}_{12}' = \langle\tilde{\psi}|D_{12}|\tilde{\psi}\rangle$, with D_{12} given by Eq. (3.14) of the text. The exact value is $I_{12} = \langle\psi_0|\delta(\vec{r})|\psi_0\rangle = \langle\psi_0|D_{12}|\psi_0\rangle = 0.10636$ a.u.

(a)

Number of parameters	$\tilde{I}_1$ Value (a.u.)	Error	$\tilde{I}_1'$ Value (a.u.)	Error
1	1.5296	16%	1.6996	6.1%
3	1.7878	1.3%	1.8146	0.23%

(b)

Number of parameters	$\tilde{I}_{12}$ Value (a.u.)	Error	$\tilde{I}_{12}'$ Value (a.u.)	Error
1	0.1912	80%	0.07874	26%
3	0.1153	8.4%	0.1070	0.6%

values. Moreover, the three-parameter value I'_{12} is more accurate than the six-parameter value $I_{12}=0.1151$ a.u. and even the ten-parameter value $I_{12}=0.1087$ a.u., while the three-parameter value I'_1 exceeds the six-parameter value $I'_1 \simeq 1.8167$ a.u. in accuracy.

IV. RELATIVISTIC ELECTRONS AND PARITY NONCONSERVING CONTACT INTERACTIONS

In this section we shall generalize the results of the preceding sections in a number of ways. First, the atomic wave functions $\Psi=\Psi(\vec{r}_1,\ldots,\vec{r}_N)$ will be regarded as $4N$-component Dirac-type spinors satisfying

$$H\Psi=\mathcal{E}\Psi\,, \tag{4.1}$$

where

$$H=\sum_{i=1}^{N}(\vec{\alpha}_i\cdot\vec{p}_i+\beta_i m)+V^{\mathrm{tot}} \tag{4.2}$$

and V^{tot} represents a sum of (parity-conserving) electron-nucleus and electron-electron interactions. Second, we shall study the evaluation of operators of the form

$$\mathcal{O}\delta(\vec{r}_i)\,,\quad \mathcal{O}\delta(\vec{r}_{ij})\,, \tag{4.3}$$

where $\mathcal{O}$ is a Dirac matrix, or a product of Dirac matrices referring to different particles. Finally, we shall consider matrix elements of such operators taken between different eigenfunctions of (4.2).

Off-diagonal matrix elements of operators of the type (4.3) enter the calculation of the parity mixing of atomic states arising from the weak neutral current. It is interesting to note that while the usual δ-function interactions in atomic physics arise only as nonrelativistic approximations to photon exchange, the δ-function interactions coming from the weak neutral current are present independently of such approximations. It is only necessary that the mass of the exchanged Z^0 boson is much larger than all electron momenta which have appreciable probability.

In the approximation in which the nucleus is treated as an infinitely massive point source, with total spin $\vec{S}_{\mathrm{nuc}}$, the parity-violating part $H^{\mathrm{pv}}_{e\text{-}N}$ of the weak electron-nucleus interaction takes the form[6]

$$H^{\mathrm{pv}}_{e\text{-}N}=\frac{G_F}{\sqrt{2}}\sum_{i=1}^{N}(\bar{c}_1\gamma_i^5-\bar{c}_2\vec{\alpha}_i\cdot\vec{S}_{\mathrm{nuc}})\delta(\vec{r}_i)$$

$$=\sum_{i=1}^{N}H^{\mathrm{pv}}_{e\text{-}N}(i)\,, \tag{4.4}$$

where γ_i^5 and $\vec{\alpha}_i$ are the usual Dirac matrices ($\vec{\alpha}=\gamma^5\vec{\sigma}$) acting on the spinor indices associated with the electron i and $\bar{c}_1$ and $\bar{c}_2$ are numerical coefficients whose value depends on both the nucleus and the underlying weak-interaction theory.[7] The parity-violating part $H^{\mathrm{pv}}_{e\text{-}e}$ of the weak electron-electron interaction has the form

$$H^{\mathrm{pv}}_{e\text{-}e}=\frac{G_F}{\sqrt{2}}c_e\sum_{i<j}^{N}[(\gamma_i^5-\vec{\sigma}_i\cdot\vec{\alpha}_j)+(\gamma_j^5-\vec{\sigma}_j\cdot\vec{\alpha}_i)]\delta(\vec{r}_{ij})$$

$$=\sum_{i<j}^{N}H^{\mathrm{pv}}_{e\text{-}e}(i,j)\,, \tag{4.5}$$

where c_e is a numerical constant and $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$.

We shall therefore mainly be interested in matrix elements of operators of the type (4.3), with $\mathcal{O}=\gamma_1^5$ or $\vec{\alpha}_1$ for $\delta(\vec{r}_1)$ and $\mathcal{O}=\gamma_1^5-\vec{\sigma}_1\cdot\vec{\alpha}_2$ for $\delta(\vec{r}_{12})$. We shall consider these in turn in Secs. IV A and IV B. We shall also briefly consider the case $\mathcal{O}=1$ in order to obtain a relativistic generalization of the identities derived in Sec. II.

A. Electron-nucleus parity-violating contact interactions

1. Relevant identities

Let us define

$$M^5_{ab}=\langle\Psi_a|\gamma_1^5\delta(\vec{r}_1)|\Psi_b\rangle \tag{4.6}$$

and

$$\vec{M}_{ab}=\langle\Psi_a|\vec{\alpha}_1\delta(\vec{r}_1)|\Psi_b\rangle\,, \tag{4.7}$$

where Ψ_a and Ψ_b are (completely antisymmetric) solutions of (4.1), with eigenvalues $\mathcal{E}_a$ and $\mathcal{E}_b$, respectively, necessarily of opposite parity. To obtain forms of M^5 and $\vec{M}$ which involve distributed operators rather than δ functions we may proceed, for example, as follows. Let $\vec{\mathcal{O}}=(\mathcal{O}^1,\mathcal{O}^2,\mathcal{O}^3)$ denote a vector whose components $\mathcal{O}^i$ are *constant* 4×4 matrices, and let

$$\vec{f}_1=-\vec{\nabla}_1 r_1^{-1}=\vec{r}_1/r_1^3\,. \tag{4.8}$$

We consider the commutator

$$[\vec{\alpha}_1\cdot\vec{p}_1,\vec{\mathcal{O}}\cdot\vec{f}_1]=\alpha_1^i\mathcal{O}^j[p_1^i,f_1^j]+[\alpha_1^i,\mathcal{O}^j]f_1^j p_1^i\,. \tag{4.9}$$

On use of the relation

$$\nabla_1^i\nabla_1^j r_1^{-1}=-\tfrac{4}{3}\pi\delta^{ij}\delta(\vec{r}_1)+T_1^{ij}\,, \tag{4.10}$$

where

$$T_1^{ij}=(3r_1^i r_1^j-\delta^{ij}r_1^2)/r_1^5 \tag{4.11}$$

we get

$$[\vec{\alpha}_1\cdot\vec{p}_1,\vec{\mathcal{O}}\cdot\vec{f}_1]=-\tfrac{4}{3}\pi i\vec{\alpha}_1\cdot\vec{\mathcal{O}}\,\delta(\vec{r}_1)+i\alpha_1^i\mathcal{O}^j T_1^{ij}$$
$$+[\alpha_1^i,\mathcal{O}^j]f_1^j p_1^i\,. \tag{4.12}$$

If we take $\vec{\mathcal{O}}=\vec{\sigma}_1$ we find on using the relations

$$\vec{\alpha}_1\cdot\vec{\sigma}_1=3\gamma_1^5\,,\quad \alpha_1^i\sigma_1^j T_1^{ij}=0\,,\quad [\alpha_1^i,\sigma_1^j]=2i\epsilon^{ijk}\alpha_1^k\,, \tag{4.13}$$

in (4.12), that

$$[\vec{\alpha}_1 \cdot \vec{p}_1, \vec{\sigma}_1 \cdot \vec{f}_1] = -4\pi i \gamma_1^5 \delta(\vec{r}_1) - 2i\vec{\alpha}_1 \cdot \vec{l}_1/r_1^3, \quad (4.14)$$

where $\vec{l}_1 = \vec{r}_1 \times \vec{p}_1$. Since, with H given by (4.2)

$$[H, \vec{\sigma}_1 \cdot \vec{f}_1] = [\vec{\alpha}_1 \cdot \vec{p}_1, \vec{\sigma}_1 \cdot \vec{f}_1] + [V^{\rm tot}, \vec{\sigma}_1 \cdot \vec{f}_1] \quad (4.15)$$

we get, on taking the matrix element of (4.15) with Ψ_a and Ψ_b and using (4.14), the identity

$$\begin{aligned} M^5_{ab} = (i/4\pi)[&(\mathcal{E}_a - \mathcal{E}_b)\langle\Psi_a|\vec{\sigma}_1 \cdot \vec{r}_1/r_1^3|\Psi_b\rangle \\ &+ 2i\langle\Psi_a|\vec{\alpha}_1 \cdot \vec{l}_1/r_1^3|\Psi_b\rangle \\ &- \langle\Psi_a|[V^{\rm tot}, \vec{\sigma}_1 \cdot \vec{r}_1/r_1^3]|\Psi_b\rangle]. \end{aligned} \quad (4.16)$$

If $\vec{\mathcal{O}}$ commutes with $\vec{\alpha}_1$, e.g., if $\vec{\mathcal{O}} = \vec{S}_{\rm nuc}$, then the last term in (4.12) vanishes and we infer

$$\begin{aligned} [\vec{\alpha}_1 \cdot \vec{p}_1, \vec{r}_1/r_1^3] = &-\tfrac{4}{3}\pi i \vec{\alpha}_1 \delta(\vec{r}_1) \\ &+ i(3\vec{\alpha}_1 \cdot \hat{r}_1 \hat{r}_1 - \vec{\alpha}_1)/r_1^3. \end{aligned} \quad (4.17)$$

On using the analog of (4.15) with $\vec{\sigma}_1 \cdot \vec{f}_1$ replaced by $\vec{f}_1$ we get the identity

$$\begin{aligned} \vec{M}_{ab} = \frac{3i}{4\pi}[&(\mathcal{E}_a - \mathcal{E}_b)\langle\Psi_a|\vec{r}_1/r_1^3|\Psi_b\rangle \\ &- i\langle\Psi_a|(3\vec{\alpha}_1 \cdot \hat{r}_1 \hat{r}_1 - \vec{\alpha}_1)/r_1^3|\Psi_b\rangle \\ &- \langle\Psi_a|[V^{\rm tot}, \vec{r}_1/r_1^3]|\Psi_b\rangle]. \end{aligned} \quad (4.18)$$

Equations (4.16) and (4.18) exhibit the quantities of interest in terms of matrix elements of distributed operators.

2. *Application to parity-mixing calculations*

Given any approximate relativistic wave functions $\tilde{\Psi}_a$ and $\tilde{\Psi}_b$ for the atomic states the forms (4.16) and (4.18) can be used to calculate the parity-mixing matrix elements and compared with the direct evaluation which requires accurate knowledge of the wave functions near the nucleus.[8] Such a comparison will give some indication of the accuracy of either calculation. Here we shall only consider the further use to which the identities (4.16) and (4.18) can be put in the case where one makes the simplest kind of central-field approximation. If the interaction $V^{\rm tot}$ in (4.2) is replaced by a sum of one-body operators,

$$V^{\rm tot} \to \tilde{U}^{\rm tot} = \sum_{i=1}^{N} \tilde{U}(i), \quad (4.19)$$

where $\tilde{U}(i)$ is an effective potential acting on the ith electron, the calculation of parity-mixing effects of course undergoes magnificent simplifications. The amplitude for the absorption of a photon of momentum $\vec{k}$ by an atom, making a transition from a state $|i\rangle$ to a state $|f\rangle$ of the same parity, then gets a contribution from parity mixing which is proportional to

$$\begin{aligned} \tilde{M}_{\rm mix} = &\sum_n \frac{\langle\tilde{\psi}_f|H^{\rm pv}_{e\text{-}N}(1)|\tilde{\psi}_n\rangle\langle\tilde{\psi}_n|\mathcal{R}_1|\tilde{\psi}_i\rangle}{\tilde{E}_f - \tilde{E}_n} \\ &+ \sum_n \frac{\langle\tilde{\Psi}_f|\mathcal{R}_1|\tilde{\Psi}_n\rangle\langle\tilde{\Psi}_n|H^{\rm pv}_{e\text{-}N}(1)|\tilde{\Psi}_i\rangle}{\tilde{E}_i - \tilde{E}_n}. \end{aligned} \quad (4.20)$$

Here the $\tilde{\psi}_n$ are single-particle Dirac wave functions satisfying

$$\tilde{H}(1)\tilde{\psi}_n(\vec{r}_1) = E_n\tilde{\psi}_n(\vec{r}_1), \quad \tilde{H}(1) \equiv \vec{\alpha}_1 \cdot \vec{p}_1 + \beta_1 m + \tilde{U}(1); \quad (4.21)$$

and $\mathcal{R}_1 = \vec{\alpha}_1 \cdot \vec{\epsilon}\exp(i\vec{k} \cdot \vec{r}_1)$ is the relativistic radiation operator; the sum on n is over a complete set of solutions of (4.21) and hence includes those with negative energy.

Following a method exploited by Sternheimer,[9] we define wave functions

$$\begin{aligned} |I\rangle &= \sum_{n \neq f} \frac{|n\rangle\langle n|\mathcal{R}_1|i\rangle}{\tilde{E}_f - \tilde{E}_n}, \\ |F\rangle &= \sum_{n \neq i} \frac{|n\rangle\langle n|\mathcal{R}_1|f\rangle}{\tilde{E}_i - \tilde{E}_n} \end{aligned} \quad (4.22)$$

which satisfy the inhomogeneous equations

$$\begin{aligned} [\tilde{E}_f - \tilde{H}(1)]|\tilde{I}\rangle &= \mathcal{R}_1\tilde{\psi}_i - \langle f|\mathcal{R}_1|i\rangle\tilde{\psi}_f, \\ [\tilde{E}_i - \tilde{H}(1)]|\tilde{F}\rangle &= \mathcal{R}_1\tilde{\psi}_f - \langle i|\mathcal{R}_1|f\rangle\tilde{\psi}_i. \end{aligned} \quad (4.23)$$

It follows that

$$\tilde{M}_{\rm mix} = \langle\tilde{\psi}_f|H^{\rm pv}_{e\text{-}N}(1)|\tilde{I}\rangle + \langle\tilde{F}|H^{\rm pv}_{e\text{-}N}(1)|\tilde{\psi}_i\rangle \quad (4.24)$$

which still involves values of wave functions at the point $\vec{r}_1 = 0$. To illustrate the use of our identities in this context let us specialize (4.16) to the one-electron case with wave functions satisfying (4.21), when it takes the form,

$$\begin{aligned} \langle\tilde{\psi}_m|\gamma_1^5\delta(\vec{r}_1)|\tilde{\psi}_n\rangle = &(\tilde{E}_m - \tilde{E}_n)\langle\tilde{\psi}_m|i\vec{\sigma}_1 \cdot \vec{r}_1/4\pi r_1^3|\tilde{\psi}_n\rangle \\ &+ \langle\tilde{\psi}_m|A_1|\tilde{\psi}_n\rangle, \end{aligned} \quad (4.25)$$

where

$$A_1 = -\vec{\alpha}_1 \cdot \vec{l}_1/2\pi r_1^3 - i[\tilde{U}(1), \vec{\sigma}_1 \cdot \vec{r}_1/4\pi r_1^3]. \quad (4.26)$$

Similarly, (4.18) takes the form

$$\begin{aligned} \langle\tilde{\psi}_m|\vec{\alpha}_1\delta(\vec{r}_1)|\tilde{\psi}_n\rangle = &(\tilde{E}_m - \tilde{E}_n)\langle\tilde{\psi}_m|3i\vec{r}_1/4\pi r_1^3|\tilde{\psi}_n\rangle \\ &+ \langle\tilde{\psi}_m|\vec{B}_1|\tilde{\psi}\rangle, \end{aligned} \quad (4.27)$$

where

$$\vec{B}_1 = 3(3\vec{\alpha}_1 \cdot \hat{r}_1 \hat{r}_1 - \vec{\alpha}_1)/4\pi r_1^3 - 3i[\tilde{U}(1), \vec{r}_1/4\pi r_1^3]. \quad (4.28)$$

If we use (4.25) and (4.27) to rewrite $\langle\tilde{\psi}_f|H^{\rm pv}_{e\text{-}N}(1)|\tilde{\psi}_n\rangle$ and $\langle\tilde{\psi}_n|H^{\rm pv}_{e\text{-}N}(1)|\tilde{\psi}_i\rangle$ and substitute the result into (4.20) we may use closure on the terms in which the energy denominator cancels

and the definitions of $|\tilde{I}\rangle$ and $|\tilde{F}\rangle$ in the other terms, to rewrite $\tilde{M}_{\rm mix}$ in the form

$$\tilde{M}_{\rm mix}=\frac{G_F}{\sqrt{2}}[\langle\tilde{\psi}_f|[i(\bar{c}_1\vec{\sigma}_1-3\bar{c}_2\vec{S}_{\rm nuc})\cdot\vec{r}_1 r_1^{-3},\mathcal{R}_1]|\tilde{\psi}_i\rangle + \langle\tilde{\psi}_f|C_1|\tilde{I}\rangle+\langle\tilde{F}|C_1|\tilde{\psi}_i\rangle], \quad (4.29)$$

where

$$C_1=\bar{c}_1A_1-\bar{c}_2\vec{S}_{\rm nuc}\cdot\vec{B}_1. \quad (4.30)$$

The nuclear spin commutes with $\mathcal{R}_1$ so that on use of the relation $[\vec{\sigma}_1\cdot\vec{r}_1,\vec{\alpha}_1\cdot\vec{\epsilon}]=2i\vec{\alpha}_1\times\vec{r}_1\cdot\vec{\epsilon}$ Eq. (4.29) reduces to

$$\tilde{M}_{\rm mix}=\frac{G_F}{\sqrt{2}}[\langle\tilde{\psi}_f|-2\bar{c}_1\vec{\alpha}_1\times\vec{r}_1\cdot\vec{\epsilon}e^{i\vec{k}\cdot\vec{r}}|\tilde{\psi}_i\rangle + \langle\tilde{\psi}_f|C_1|\tilde{I}\rangle+\langle\tilde{F}|C_1|\tilde{\psi}_i\rangle]. \quad (4.31)$$

For the case where the effective potential $\tilde{U}(1)$ is diagonal in Dirac matrices *and* local, e.g., in the Hartree approximation, the commutator terms in both A_1 [Eq. (4.26)] and $\vec{B}_1$ [Eq. (4.28)] vanish and

$$C_1\to-\bar{c}_1\vec{\alpha}_1\cdot\vec{l}_1/2\pi r_1^3 - 3\bar{c}_2(3\vec{\alpha}_1\cdot\hat{r}_1\vec{S}_{\rm nuc}\cdot\hat{r}_1-\vec{\alpha}_1\cdot\vec{S}_{\rm nuc})/4\pi r_1^3, \quad (4.32)$$

which does not involve the effective potential explicitly. Equation (4.31) should be useful in practical calculations of parity mixing in atoms.

In this connection it may be useful to state the explicit form of the identity (4.25) in terms of the radial wave functions $g(r_1)$ and $f(r_1)$ associated with the large and small components of the Dirac spinor $\tilde{\psi}(\vec{r}_1)$. As an example we specialize (4.25) to the case of single-electron $S_{1/2}$ and $P_{1/2}$ states with wave function $\psi_s(\vec{r}_1)$ and $\tilde{\psi}_p(\vec{r}_1)$ whose general form is

$$\tilde{\psi}_s(\vec{r}_1)=\frac{1}{\sqrt{4\pi}}\begin{pmatrix}g_s\chi\\-if_s\vec{\sigma}_1\cdot\hat{r}_1\chi\end{pmatrix},\qquad \tilde{\psi}_p(\vec{r}_1)=\frac{1}{\sqrt{4\pi}}\begin{pmatrix}g_p\vec{\sigma}_1\cdot\hat{r}_1\chi'\\-if_p\chi'\end{pmatrix}, \quad (4.33)$$

where χ and χ' are two-component spinors. It follows readily from (4.25) that

$$\langle\tilde{\psi}_p|\gamma_5\delta(\vec{r}_1)|\tilde{\psi}_s\rangle=\frac{i}{4\pi}[(\tilde{E}_p-\tilde{E}_s)(\langle g_p|r_1^{-2}|g_s\rangle+\langle f_p|r_1^{-2}|f_s\rangle - 4\langle g_p|r_1^{-3}|f_s\rangle]\langle\chi'|\chi\rangle, \quad (4.34)$$

where the left-hand side of (4.34) is just equal to $if_p^*(0)g_s(0)\langle\chi'|\chi\rangle/4\pi$. For the case at hand, Eq. (4.27) assumes the same form with the factor $\langle\chi'|\chi\rangle$ replaced by $\langle\chi'|\vec{\sigma}|\chi\rangle$.

In the foregoing, we have used the central-field approximation for the sake of concreteness and to illustrate the use of identities (4.16) and (4.18) in a context in which practical calculations have already been performed. However, it must be emphasized that these identities hold independently of this approximation and could therefore also be used, in a similar way, in calculations of parity mixing in which corrections to the central-field approximations are included[10] or, more generally, in which wave functions which include correlation are used. Applications of these identities to such calculations in specific atoms will be reported elsewhere.

B. Electron-electron parity-violating contact interaction

The matrix element of $H_{e\text{-}e}^{\rm pv}(1,2)$ between eigenstates Ψ_a and Ψ_b is given [see (4.5)] by

$$\langle\Psi_a|H_{e\text{-}e}^{\rm pv}(1,2)|\Psi_b\rangle=\frac{G_F}{\sqrt{2}}c_e\langle\Psi_a|\Gamma_{12}^5\delta(\vec{r})|\Psi_b\rangle \equiv\frac{G_F}{\sqrt{2}}c_eL_{ab}, \quad (4.35)$$

where $\vec{r}=\vec{r}_1-\vec{r}_2$ and

$$\Gamma_{12}^5=(\gamma_1^5+\gamma_2^5)(1-\vec{\alpha}_1\cdot\vec{\alpha}_2)=\gamma_1^5+\gamma_2^5-\vec{\sigma}_1\cdot\vec{\alpha}_2-\vec{\alpha}_1\cdot\vec{\sigma}_2. \quad (4.36)$$

To "desensitize" L_{ab} we need to find some identities analogous to (4.14) and (4.17). We note first that with $\vec{\mathcal{O}}$ a constant matrix vector and $\vec{f}$ defined by

$$\vec{f}=\vec{r}/r^3 \quad (4.37)$$

we have, in analogy with (4.12)

$$[\vec{\alpha}_1\cdot\vec{p}_1,\vec{\mathcal{O}}\cdot\vec{f}]=-\tfrac{4}{3}\pi i\vec{\alpha}_1\cdot\vec{\mathcal{O}}\delta(\vec{r})+i\alpha_1^i\mathcal{O}^jT^{ij} + [\alpha_1^i,\mathcal{O}^j]f^jp_1^i, \quad (4.38)$$

$$[\vec{\alpha}\cdot\vec{p}_2,\vec{\mathcal{O}}\cdot\vec{f}]=+\tfrac{4}{3}\pi i\vec{\alpha}_2\cdot\vec{\mathcal{O}}\delta(\vec{r})-i\alpha_2^i\mathcal{O}^jT^{ij} + [\alpha_2^i,\mathcal{O}^j]f^jp_2^i, \quad (4.39)$$

where

$$T^{ij}=(3r^ir^j-\delta^{ij}r^2)/r^5. \quad (4.40)$$

On putting $\vec{\mathcal{O}}=\vec{\sigma}_1$ and then $\vec{\mathcal{O}}=-\vec{\sigma}_2$ in both (4.38) and (4.39) and adding the resulting four equations one gets

$$[\vec{\alpha}_1\cdot\vec{p}_1+\vec{\alpha}_2\cdot\vec{p}_2,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{f}] =-4\pi i(\gamma_1^5+\gamma_2^5)(1-\tfrac{1}{3}\vec{\alpha}_1\cdot\vec{\alpha}_2)\delta(\vec{r}) + i(\gamma_1^5+\gamma_2^5)s/r^3-2iP_{12}, \quad (4.41)$$

where

$$s=\vec{\sigma}_1\cdot\vec{\sigma}_2-3\vec{\sigma}_1\cdot\hat{r}\vec{\sigma}_2\cdot\hat{r} \quad (4.42)$$

is the tensor operator and

$$P_{12}=\vec{\alpha}_1\cdot\vec{f}\times\vec{p}_1-\vec{\alpha}_2\cdot\vec{f}\times\vec{p}_2. \quad (4.43)$$

The matrix multiplying $\delta(\vec{r})$ in (4.41) is not quite Γ_{12}^5, needed in (4.35). However, if we also put

$\vec{\sigma}=i\vec{\sigma}_1\times\vec{\sigma}_2$ in (4.38) and (4.39) and again add the resulting equations we get

$$[\vec{\alpha}_1\cdot\vec{p}_1+\vec{\alpha}_2\cdot\vec{p}_2, i\vec{\sigma}_1\times\vec{\sigma}_2\cdot\vec{f}\,] = \tfrac{8}{3}\pi i(\gamma_1^5+\gamma_2^5)(\vec{\alpha}_1\cdot\vec{\alpha}_2)\delta(\vec{r}) - i(\gamma_1^5+\gamma_2^5)s/r^3 + 2iQ_{12}\,, \tag{4.44}$$

where

$$Q_{12}=i(\vec{\alpha}_1\cdot\vec{\sigma}_2\vec{f}\cdot\vec{p}_1-\vec{\alpha}_2\cdot\vec{\sigma}_1\vec{f}\cdot\vec{p}_2 + \vec{\alpha}_2\cdot\vec{f}\vec{\sigma}_1\cdot\vec{p}_2-\vec{\alpha}_1\cdot\vec{f}\vec{\sigma}_2\cdot\vec{p}_1)\,. \tag{4.45}$$

On adding (4.41) and (4.44) we see that with

$$h_{12}\equiv(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{f}+i(\vec{\sigma}_1\times\vec{\sigma}_2)\cdot\vec{f} \tag{4.46}$$

we have

$$[\vec{\alpha}_1\cdot\vec{p}_1+\vec{\alpha}_2\cdot\vec{p}_2, h_{12}]=(-4\pi i)\Gamma_{12}^5\delta(\vec{r})-2i(P_{12}-Q_{12})\,. \tag{4.47}$$

The identity (4.47) is an analog of (4.14) and can be used in a similar way. With H given by (4.2) we have

$$[H,h_{12}]=[\vec{\alpha}_1\cdot\vec{p}_1+\vec{\alpha}_2\cdot\vec{p}_2,h_{12}]+[V^{\rm tot},h_{12}] \tag{4.48}$$

so that on taking the matrix element of (4.48) with Ψ_a and Ψ_b and using (4.45) we get

$$L_{ab}=(i/4\pi)[(\mathcal{E}_a-\mathcal{E}_b)\langle\Psi_a|h_{12}|\Psi_b\rangle + 2i\langle\Psi_a|(P_{12}-Q_{12})|\Psi_b\rangle - \Psi_a|[V^{\rm tot},h_{12}]|\Psi_b\rangle]\,. \tag{4.49}$$

Equation (4.49) exhibits $L_{ab}=\langle\Psi_a|\Gamma_{12}^5\delta(\vec{r})|\Psi_b\rangle$ as a sum of terms involving only distributed operators and is an analog of (4.16) and (4.18). The P_{12} term is similar to the second term in (4.16). However, the Q_{12} term is of a type not encountered in the electron-nucleus interaction.

C. Nonrelativistic limits

The nonrelativistic equivalents of identities derived in the preceding sections may be useful for atoms with small enough Z. To obtain these we replaced Ψ in (4.16), (4.18), and (4.49) by

$$\Psi'=\prod_{i=1}^{N}\left(1+\frac{\vec{\alpha}_i\cdot\vec{p}_i}{2m_i}\right)\psi, \tag{4.50}$$

where ψ is the eigenfunction, with eigenvalue W, of the nonrelativistic Hamiltonian $H_{\rm nr}$ corresponding to H, and retain only the leading terms in an expansion in powers of v/c. Actually we need only use the fact that $\beta_i\psi=\psi$. Then Eq. (4.16) reduces to

$$M_{ab}^5\to\langle\psi_a|\vec{\sigma}_1\cdot\vec{p}_1\delta(\vec{r}_1)+\delta(\vec{r}_1)\vec{\sigma}_1\cdot\vec{p}_1|\psi_b\rangle/2m = \frac{i}{4\pi}(W_a-W_b)\langle\psi_a|\vec{\sigma}_1\cdot\vec{r}_1/r_1^3|\psi_b\rangle + \frac{i}{4\pi m}[\langle\vec{p}_1\phi_a|\cdot\vec{\sigma}_1\times\vec{l}_1/r_1^3|\phi_b\rangle + \langle(\vec{\sigma}_1\times\vec{l}_1/r_1^3)\phi_a|\cdot\vec{p}_1|\phi_b\rangle]\,. \tag{4.51}$$

For the special case of a single electron, with $\psi_a=R_p(r_1)\vec{\sigma}\cdot\vec{r}_1\chi/\sqrt{4\pi}$ a $P_{1/2}$ state and $\psi_b=R_s(r_1)\chi/\sqrt{4\pi}$ an $S_{1/2}$ state, Eq. (4.51) reduces, on cancellation of a factor of 4π, to

$$3R_p'(0)R_s(0)/2m=(W_p-W_s)\langle R_p|r_1^{-2}|R_s\rangle - (2/m)\langle R_p|r_1^{-3}d/dr|R_s\rangle\,. \tag{4.52}$$

Equation (4.52) coincides with a result given previously,[11] derived directly from the nonrelativistic Schrödinger equation.

Similarly, (4.49) reduces to

$$L_{ab}\to\frac{1}{2m}\langle\psi_a|(\vec{\sigma}_1\cdot\vec{p}_1+\vec{\sigma}_2\cdot\vec{p}_2)\delta(\vec{r})(1-\vec{\sigma}_1\cdot\vec{\sigma}_2)+\text{h.c.}|\psi_b\rangle = \frac{i}{4\pi}(W_a-W_b)\langle\psi_a|h_{12}|\psi_b\rangle+\cdots, \tag{4.53}$$

where the terms not written out may be obtained by making replacements such as

$$\vec{\alpha}_i g(r)\to[\vec{p}_i,g]_+ + i\vec{\sigma}_i\times[\vec{p}_i,g]/2m$$

in the terms beyond the first in (4.49).

To conclude this subsection we consider briefly a kind of inverse problem — finding relativistic analogs of the nonrelativistic identities studied in Sec. II. To be specific let us consider a single electron in an external potential $U_{\rm ex}(1)$ with wave function Φ an eigenfunction with eigenvalue $\mathcal{E}$ of

$$H_1=\vec{\alpha}_1\cdot\vec{p}_1+\beta_1 m+U_{\rm ex}(1)=H_0(1)+U_{\rm ex}(1)\,. \tag{4.54}$$

The commutator of H_1 with $\partial/\partial r_1$ does not yield an identity for $\langle\Phi|\delta(\vec{r}_1)|\Phi\rangle$, unlike the nonrelativistic case. The trick here is to consider the square of H_1,

$$H_1^2=H_0^2+[H_0,U_{\rm ex}]_+ + U_{\rm ex}^2\,, \tag{4.55}$$

and to note that

$$\left[\frac{\partial}{\partial r_1},H_1^2\right]=\frac{2}{r_1^2}\frac{\partial}{\partial r_1}-\frac{2}{r_1^2}\vec{l}_1^{\,2}+\left[H_1,\frac{\partial U_{\rm ex}}{\partial r_1}\right]_+ - [(\vec{\alpha}_1\cdot\vec{p}_1^{\,\rm tr})/r_1,U_{\rm ex}]_+ \tag{4.56}$$

where $\vec{p}_1^{\,\rm tr}=\vec{p}_1-\hat{r}_1\cdot\vec{p}_1$ is the part of $\vec{p}_1$ transverse to $\hat{r}_1$. On taking the expectation value of (4.56) with Φ we get

$$\langle\Phi|\delta(\vec{r}_1)|\Phi\rangle=\frac{\mathcal{E}}{2\pi}\langle\Phi|\frac{\partial U_{\rm ex}}{\partial r_1}|\Phi\rangle-\langle\Phi|\frac{\vec{l}_1^{\,2}}{2\pi r_1^3}|\Phi\rangle - \langle\Phi|[(\vec{\alpha}_1\cdot\vec{p}_1^{\,\rm tr})/4\pi r_1,U_{\rm ex}]_+|\Phi\rangle\,. \tag{4.57}$$

Since the last term in (4.57) is $\mathcal{O}(v^2/c^2)$ relative to the first two terms (assuming that U is, e.g., diagonal in Dirac matrices) and since $\mathcal{E} \approx m$ for $v/c \ll 1$, the nonrelativistic limit of (4.57) coincides with the identity (2.14), specialized to $N=1$.

Identities similar to (4.57) can be obtained for both $\delta(\vec{r}_1)$ and $\delta(\vec{r}_{12})$ when $N>1$, again by computing the commutator of H^2 with $\partial/\partial r_1$ and $\partial/\partial r$ and then taking the expectation value with an eigenfunction Ψ of the relativistic N-electron Hamiltonian H [Eq. (4.2)]. However, the nonrelativistic limit of these identities is not as transparent as that of (4.57).

Finally, we note another identity, similar to (4.52), given in earlier work,[11] viz.,

$$3R_p'(0)R_s(0)/2m = \langle R_p | [W_p + W_s - 2\tilde{U}_{ex}(1)]r_1^{-2} | R_s \rangle - m^{-1}\int_0^\infty dr\, R_p'(r)R_s'(r), \quad (4.58)$$

and ask for the relativistic generalization. We define

$$N_{ab} \equiv \langle \Psi_a | i\gamma_1^0\gamma_1^5\delta(\vec{r}_1) | \psi_b \rangle \quad (4.59)$$

and note the anticommutator identity

$$[H, \gamma_1^0\vec{\sigma}_1\cdot\vec{f}_1]_+ = 4\pi i\gamma_1^0\gamma_1^5\delta(\vec{r}_1) + 2i\gamma_1^0\vec{\alpha}_1\cdot\vec{l}_1/r_1^3 + 2m\vec{\sigma}_1\cdot\vec{f}_1 + [V^{tot}, \gamma_1^0\vec{\sigma}_1\cdot\vec{f}_1]_+ . \quad (4.60)$$

From (4.60) one infers that for a local diagonal V^{tot},

$$N_{ab} = (1/4\pi)[\langle \Psi_a | (E_a + E_b - 2m\gamma_1^0 - 2V^{tot})\gamma_1^0\vec{\sigma}_1\cdot\vec{f}_1 | \Psi_b \rangle - 2i\langle \Psi_a | \gamma_1^0\vec{\alpha}_1\cdot\vec{l}_1/r_1^3 | \Psi_b \rangle]. \quad (4.61)$$

On specializing to the one-particle case and going to the nonrelativistic limit, one easily sees that for the case of S and P states (4.61) reduces to (4.58).

V. SUMMARY AND DISCUSSION

A. Summary of results

The main results in Sec. II are the identities (2.13) and (2.22). These state that if ψ is an eigenfunction of a nonrelativistic N-body Hamiltonian of the general form (2.10), then $I_1 \equiv \langle \psi | \delta(\vec{r}_1) | \psi \rangle = \langle \psi | D_1^{tot} | \psi \rangle$ and $I_{12} \equiv \langle \psi | \delta(\vec{r}_{12}) | \psi \rangle = \langle \psi | D_{12}^{tot} | \psi \rangle$, where D_1^{tot} and D_{12}^{tot} are simple "distributed operators," defined by (2.15) and (2.24), each involving a term proportional to a derivative of the interaction potential V^{tot} and an angular momentum term. These identities can be regarded as generalizations of an "S-state identity" which has been used in discussions of the charmonium model. It was argued that use of the alternative forms D_1^{tot} and D_{12}^{tot} is likely to give more accurate values for I_1 and I_{12} when only approximate wave functions are available. In support of this idea it was shown in Sec. III that the contact interactions entering the $\mathcal{O}(\alpha^2 Ry)$ corrections to atomic energy levels can be very accurately evaluated by use of these identities, even with relatively crude wave functions, at least in the case of helium. As an example, a three-parameter Hylleraas wave function used with D_{12} gives a value for I_{12} which is correct to within a few tenths of a percent, a result which is better than that obtained with a ten-parameter wave function used with $\delta(\vec{r}_{12})$.

In Sec. IV, the ideas involved were extended to relativistic many-body systems, in particular to many-electron atoms and to matrix elements of the form $M_{ab}^5 = \langle \Psi_a | \gamma_1^5\delta(\vec{r}_1) | \Psi_b \rangle$ and $\vec{M}_{ab} = \langle \Psi_a | \vec{\alpha}_1\delta(\vec{r}_1) | \times \Psi_b \rangle$, where Ψ_a and Ψ_b are eigenfunctions of a relativistic Hamiltonian H of the very general form (4.2). Identities which exhibit M_{ab}^5 and $\vec{M}_{ab}$ as matrix elements of distributed operators were derived [Eqs. (4.16) and (4.18), respectively]. It was then shown how these identities can be used to ameliorate one of the difficulties encountered in the calculation of parity-mixing effects in atoms: the apparent need to have wave functions which are especially accurate at particular points in coordinate space, i.e., $\vec{r}_i = 0$ or $\vec{r}_i = \vec{r}_j$. This was illustrated in the central-field approximation, by the derivation of Eq. (4.31) for the contribution $\tilde{M}_{mix}$ to the amplitude $\gamma + \Psi_i \to \Psi_f$ arising from the parity-violation part of the weak electron-nucleus interaction (4.4). Equation (4.31) exhibits $\tilde{M}_{mix}$ in terms of distributed operators and the solutions of the inhomogeneous equations shown in (4.23). We also derived an identity (4.49) for the quantity

$$L_{ab} = \langle \Psi_a | (\gamma_1^5 + \gamma_2^5)(1 - \vec{\alpha}_1\cdot\vec{\alpha}_2)\delta(\vec{r}) | \Psi_b \rangle,$$

which may be similarly useful in the study of parity-violating effects arising from the weak electron-electron interaction (4.5). In passing, we obtained a relativistic generalization, Eq. (4.57), of the nonrelativistic identity (1.2) for $\delta(\vec{r}_1)$.

To conclude this paper we shall (i) give a physical interpretation of the $\delta(\vec{r}_1)$ identity and (ii) discuss briefly the question of the inclusion of the effects of virtual electron-positron pairs in calculations of parity violation.

B. Physical interpretation of the identity for $\delta(\vec{r}_1)$

It is interesting to compare the identities (1.7) and (1.8) for $l=0$ and $l\neq 0$, respectively. The identity (1.8) for $l\neq 0$ states admits a simple physical interpretation. It may be rewritten in the form

$$\langle\phi_l|F_r^{\rm op}|\phi_l\rangle=0 \quad (l\neq 0), \tag{5.1}$$

where

$$F_r^{\rm op}=\frac{-\partial V}{\partial r}+\frac{\vec{l}_{\rm op}^{\,2}}{\mu r^3}. \tag{5.2}$$

Now for a particle of mass μ moving with angular momentum $\vec{l}$ in a central field $V(r)$, the radial equation of motion is just

$$F_r^{\rm class}=\mu\ddot{r}, \tag{5.3}$$

where

$$F_r^{\rm class}=\frac{-\partial V}{\partial r}+\frac{\vec{l}^{\,2}}{\mu r^3}. \tag{5.4}$$

For a closed orbit

$$\bar{\ddot{r}}=0, \tag{5.5}$$

where the bar denotes the time average over a complete cycle. It follows that

$$\bar{F}_r^{\rm class}=0, \tag{5.6}$$

and hence (5.1) is just the quantum equivalent, for a stationary state, of (5.6) for a closed classical orbit. However, this interpretation seems to fail for S states ϕ_0 since, with definition (5.2), the identity (1.7) has the form

$$\langle\phi_0|F_r^{\rm op}|\phi_0\rangle=(-2\pi/\mu)|\phi_0(0)|^2. \tag{5.7}$$

The interpretation can be extended to S states if we note that the operator $F_r^{\rm op}$ is *not* the appropriate quantum equivalent of $F_r^{\rm class}$ in all cases. To see this, let us define $\mathfrak{F}_r^{\rm op}$ by

$$\mathfrak{F}_r^{\rm op}=\mu\ddot{r}_{\rm op}, \tag{5.8}$$

where $\ddot{r}_{\rm op}\equiv i[H,\dot{r}_{\rm op}]$ and $\dot{r}_{\rm op}\equiv i[H,r]$ so that

$$\ddot{r}_{\rm op}=-[H,[H,r]]. \tag{5.9}$$

From $\dot{r}_{\rm op}=(\hat{r}\cdot\vec{p}+\vec{p}\cdot\hat{r})/2\mu=(\hat{r}\cdot\vec{p}-ir^{-1})/\mu$ we see that $\mathfrak{F}_r^{\rm op}=i[H,\hat{r}\cdot\vec{p}-ir^{-1}]$ and hence that $\mathfrak{F}_r^{\rm op}$ will contain a contact term given by $-\vec{\nabla}^2r^{-1}/2\mu=2\pi\delta(\vec{r})/\mu$. Thus one finds

$$\mathfrak{F}_r^{\rm op}=F_r^{\rm op}+2\pi\delta(\vec{r})/\mu. \tag{5.10}$$

It follows that both the $l=0$ and $l\neq 0$ identities may be uniformly written in the form

$$\langle\phi_l|\mathfrak{F}_r^{\rm op}|\phi_l\rangle=0 \tag{5.11}$$

if one takes into account the nonclassical contact term in $\mathfrak{F}_r^{\rm op}$. The fact that this term has its origin in quantum mechanics can be made clear by noting that we have been using units in which $\hbar=1$. In the usual units, the contact term has the form $2\pi\hbar^2\delta(\vec{r})/\mu$, which vanishes for $\hbar\to 0$.

C. Pair effects in calculations of parity violation

We have deliberately refrained from specifying the form of $V^{\rm tot}$ in the relativistic Hamiltonian

$$H=\sum_{i=1}^{N}(\vec{\alpha}_i\cdot\vec{p}_i+\beta_i m)+V^{\rm tot} \tag{5.12}$$

in our derivation of identities relevant for the calculation of parity-violating effects in atoms. The usual choice for $N>1$ is

$$V^{\rm tot}=\sum_{i=1}^{N}U_{\rm ex}(i)+\sum_{i<j}^{N}\frac{e^2}{r_{ij}}, \tag{5.13}$$

where $U_{\rm ex}(i)$ is the electron-nucleus interaction. However, the Hamiltonian (5.12) then has no bound states.[12] When electron-electron interaction is included one must be careful in applying the prescriptions of hole theory rather than one-electron theory. Within the framework of the central-field approximation these problems are not manifest, but they must be faced as soon as one wishes to go beyond this approximation. A practical formalism which avoids such difficulties does exist. It is based on a modified Dirac-Coulomb Hamiltonian, derivable from quantum electrodynamics, in which the interactions terms are sandwiched between positive-energy projection operators and effects involving virtual electron-positron pairs can be treated systematically by perturbation theory.[12] Effects of transverse-photon exchange, as represented by the Breit operator, may also be included in zero order without encountering spurious higher-order terms. This approach has been used successfully in a number of different physical problems[12,13] and should be useful in including pair terms in the calculation of parity-violating effects in atomic physics.[14]

Added note: After completion of this work some related papers were brought to our attention. Equation (1.8) can be regarded as a special case of a more general equation for the matrix element of r^n between radial wave functions, derived by D. E. Hughes, J. Phys. B 10, 3167 (1977). More accurate values of $\langle\delta(\vec{r}_1)\rangle$ for helium than one gets from direct evaluation with a variational wave function have also been obtained by other techniques. See, e.g., A. Dalgarno and A. L. Stewart, Proc. R. Soc. London Ser. A 257, 534 (1960) and C. Schwartz, Ann. Phys. (N.Y.) 6, 156 (1959); *ibid.* 6, 170 (1960).

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APPENDIX A: EVALUATION OF I_1' AND I_{12}' FOR HELIUM

In terms of the Hylleraas variables $s=r_1+r_2$, $t=r_1-r_2$, and $u=r_{12}$ the potential term in (3.9)

takes the form

$$V^{\rm tot}=-\frac{8\alpha s}{s^2-t^2}+\frac{\alpha}{u}, \tag{A1}$$

where Z has been taken to be 2. The derivatives required for D_1 and D_{12} then become

$$\frac{\partial V^{\rm tot}}{\partial r_1}=\frac{8\alpha}{(s+t)^2}-\alpha\frac{st+u^2}{u^3(s+t}} \tag{A2}$$

and

$$\frac{\partial V^{\rm tot}}{\partial r}=8\alpha s\frac{u^2(s^2+3t^2)-t^2(3s^2+t^2)}{u(s^2-t^2)^3}-\frac{\alpha}{u^2}. \tag{A3}$$

Although $\vec{1}_1^{\,2}$ and $\vec{1}^{\,2}$ may be expressed in terms of derivatives involving s, u, t, and angular variables, for our purposes it is simpler to evaluate $\vec{1}_1^{\,2}\psi(s,u,t)$ and $\vec{1}^{\,2}\psi(s,u,t)$ directly by use of the chain rule. This gives

$$\vec{1}_1^{\,2}\psi(s,u,t)=\tfrac{1}{2}(s^2+t^2-2u^2)\frac{1}{u}\frac{\partial\psi}{\partial u}-\tfrac{1}{4}(s^2-u^2)(t^2-u^2)\frac{1}{u}\frac{\partial}{\partial u}\left(\frac{1}{u}\frac{\partial\psi}{\partial u}\right) \tag{A4}$$

and

$$\vec{1}^{\,2}\psi(s,u,t)=\frac{2st}{s^2-t^2}\left(s\frac{\partial\psi}{\partial t}-t\frac{\partial\psi}{\partial s}\right)+\frac{(s^2-u^2)(t^2-u^2)}{(s^2-t^2)^3}\left(t(3s^2+t^2)\frac{\partial\psi}{\partial t}-s(s^2+3t^2)\frac{\partial\psi}{\partial s}\right)+\frac{(s^2-u^2)(t^2-u^2)}{(s^2-t^2)^2}\left(t^2\frac{\partial^2\psi}{\partial s^2}-2st\frac{\partial^2\psi}{\partial t\partial s}+s^2\frac{\partial^2\psi}{\partial t^2}\right). \tag{A5}$$

With a volume element $d\tau=\pi^2u(s^2-t^2)ds\,du\,dt$ and ψ real, the expressions in Eq. (3.12) for I_1' and I_{12}' then take the form

$$I_1'=\frac{\pi}{2}\int_0^\infty ds\int_0^s du\int_{-u}^u dt\,u(s-t)\left[\alpha m\left(\frac{8}{s+t}-\frac{st+u^2}{u^3}\right)\psi^2-\frac{8\psi\vec{1}_1^{\,2}\psi}{(s+t)^2}\right] \tag{A6}$$

and

$$I_{12}'=\frac{\pi}{4}\int_0^\infty ds\int_0^s du\int_{-u}^u dt\left(8\alpha ms\frac{u^2(s+3t^2)-t^2(3s^2+t^2)}{(s^2-t^2)^2}\psi^2-\alpha m\frac{s^2-t^2}{u}\psi^2-2\frac{s^2-t^2}{u^2}\psi\vec{1}^{\,2}\psi\right). \tag{A7}$$

The Hylleraas ansatz for ψ is

$$\psi=Ne^{-\kappa s/2}\sum_a C_a\kappa^{n+2l+m}s^nt^{2l}u^m, \tag{A8}$$

where $a=(n,2l,m)$ with integer n, l, and m, N is a normalization constant, and κ and C_a are variational parameters. Substitution of (A8) into (A6) yields

$$I_1'=\pi\frac{N^2}{k^3}\sum_{a,a'}C_aC_{a'}S_1^{aa'}, \tag{A9}$$

where $S_1^{aa'}$ denotes a sum of integrals each of which can be done analytically; I_{12}' may be written similarly in terms of a matrix $S_{12}^{aa'}$. The expressions for these quantities, which are conveniently taken to be symmetric in the superscripts, are too lengthy to be recorded here.[15]

APPENDIX B: ERROR BOUNDS FOR I_1 AND I_{12} FOR HELIUM

The Hamiltonian is $H=K+V_{\rm tot}$ where, with $\vec{r}=\vec{r}_1-\vec{r}_2$, $\vec{R}=\frac{1}{2}(\vec{r}_1+\vec{r}_2)$, $\vec{\nabla}=i^{-1}\partial/\partial\vec{r}$, and $\vec{\nabla}_R=i^{-1}\partial/\partial\vec{R}$, K is given by (a.u.)

$$K=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2=-\nabla^2-\tfrac{1}{4}\nabla_R^2. \tag{B1}$$

Let ψ be the *exact* ground-state eigenfunction of H and let $\tilde{\psi}$ be an approximation to ψ. One can then write approximations $\tilde{I}_1$ and $\tilde{I}_{12}$ for I_1 and I_{12} as

$$\tilde{I}_1\equiv\langle\tilde{\psi}\,|\,\delta(\vec{r}_1)\,|\,\tilde{\psi}\rangle\quad\text{and}\quad\tilde{I}_{12}\equiv\langle\tilde{\psi}\,|\,\delta(\vec{r})\,|\,\tilde{\psi}\rangle. \tag{B2}$$

The errors ϵ_1 and ϵ_{12} are defined by

$$\epsilon_1=|\tilde{I}_1-I_1|,\quad\text{and}\quad\epsilon_{12}=|\tilde{I}_{12}-I_{12}|. \tag{B3}$$

A practical formula for an upper bound on ϵ_1 has been given by Rédei.[4] We sketch the essential steps in his treatment and then indicate the modifications needed for ϵ_{12}.

The approximate wave function is written in the form

$$\psi=(1-\eta^2)^{1/2}\psi+\eta f, \tag{B4}$$

where η is chosen to be real and positive and ψ and f are orthonormal,

$$\langle\psi\,|\,\psi\rangle=\langle f\,|f\rangle=1,\quad\langle\psi|f\rangle=0.$$

An upper bound on η^2 is provided by

$$\eta^2\leq\eta_{\rm max}^2\equiv(\tilde{E}_0-E_0)/(E_1-E_0), \tag{B5}$$

where $\tilde{E}_0\equiv\langle\tilde{\psi}\,|\,H\,|\,\tilde{\psi}\rangle$ and E_0 and E_1 are exact eigenvalues for the ground state and the next highest state of the same symmetry. Using Schwartz's inequality, Rédei derives another inequality [his Eq. (10)], a special case of which is

$$|(1-\eta^2)I_1-\tilde{I}_1|\leq 2\eta\tilde{I}_1^{1/2}\langle f\,|\,\delta(\vec{r}_1)\,|\,f\rangle^{1/2}+\eta^2\langle f\,|\,\delta(\vec{r}_1)\,|\,f\rangle. \tag{B6}$$

Next an upper bound for $\langle f|\delta(\vec{r}_1)|f\rangle$ is found. The bound

$$\langle f|\delta(\vec{r}_1)|f\rangle \leq \frac{3}{2\pi}\langle \nabla_1^2 f|\nabla_1^2 f\rangle^{1/2}\langle f|-\nabla_1^2|f\rangle^{1/2}, \quad \text{(B7)}$$

not written down by Rédei, but implicit in his equations, is then used to show that

$$\langle f|\delta(\vec{r}_1)|f\rangle \leq \frac{3\sqrt{2}}{2\pi}\langle Kf|Kf\rangle^{1/2}\langle f|K|f\rangle^{1/2}. \quad \text{(B8)}$$

These inequalities are independent of the definition of the function f. Further inequalities which depend on the definition (B4) of f and the form of $H=K+V^{\text{tot}}$ that give upper bounds for $\eta\langle f|K|f\rangle^{1/2}$ and $\eta\langle Kf|Kf\rangle^{1/2}$ can now be used. These bounds, derived by Kinoshita,[16] are

$$\eta\langle f|K|f\rangle^{1/2} \leq B \equiv 2\eta_{\max} + [\eta_{\max}^2(E_0+4) + (\tilde{E}_0 - E_0)]^{1/2} \quad \text{(B9)}$$

and

$$\eta\langle Kf|Kf\rangle^{1/2} \leq C/[3\sqrt{2}/2\pi)B] \equiv \sqrt{44}B + [\sigma^2 + \tilde{E}_0^2 - (1-\eta_{\max}^2)E_0^2]^{1/2}, \quad \text{(B10)}$$

where

$$\sigma^2 \equiv \langle\tilde{\psi}|H^2|\tilde{\psi}\rangle - \tilde{E}_0^2. \quad \text{(B11)}$$

The use of (B6), (B8), (B9), and (B10) then gives the final result[4]

$$\epsilon_1 \leq \epsilon_1^{\max} \equiv \frac{1}{1-\eta_{\max}^2}(2C^{1/2}\tilde{I}_1^{1/2} + C + \eta_{\max}^2\tilde{I}_1). \quad \text{(B12)}$$

In order to derive the analogous bound $\epsilon_{12}^{\max}$ for ϵ_{12} we begin by making the obvious replacements in (B6) to give

$$|(1-\eta^2)I_{12} - \tilde{I}_{12}| \leq 2\eta\tilde{I}_{12}^{1/2}\langle f|\delta(\vec{r})|f\rangle^{1/2} + \eta^2\langle f|\delta(\vec{r})|f\rangle. \quad \text{(B13)}$$

One can find an upper bound for $\langle f|\delta(\vec{r})|f\rangle$, which corresponds to that in (B7), by following the procedure of Rédei. Repeated integration by parts yields

$$\langle f|\delta(\vec{r})|f\rangle = -\frac{1}{4\pi}\int\frac{1}{r}\nabla^2|f|^2\,d\vec{r}\,d\vec{R}.$$

Use of the relation $\nabla^2|f|^2 = 2\mathrm{Re}(f^*\nabla^2 f) + 2|\vec{\nabla}f|^2$ and the triangle inequality give

$$\langle f|\delta(\vec{r})|f\rangle \leq \frac{1}{2\pi}\left|\int\frac{1}{r}f^*\nabla^2 f\,d\vec{r}\,d\vec{R}\right| + \frac{1}{2\pi}\int\frac{1}{r}|\vec{\nabla}f|^2\,d\vec{r}\,d\vec{R}. \quad \text{(B14)}$$

We now use, as in Ref. 4, the following inequalities

$$\left|\int\frac{1}{r}f^*\nabla^2 f\,d\vec{r}\,d\vec{R}\right| \leq 2\langle\nabla^2 f|\nabla^2 f\rangle^{1/2}\langle f|-\nabla^2|f\rangle,$$

$$\int\frac{1}{r}|\vec{\nabla}f|^2\,d\vec{r}\,d\vec{R} \leq \langle\nabla^2 f|\nabla^2 f\rangle^{1/2}\langle f|-\nabla^2|f\rangle.$$

From these one can see that, just as in (B7),

$$\langle f|\delta(\vec{r})|f\rangle \leq \frac{3}{2\pi}\langle\nabla^2 f|\nabla^2 f\rangle^{1/2}\langle f|-\nabla^2|f\rangle^{1/2}. \quad \text{(B15)}$$

To put this upper limit in a form analogous to (B8), consider the obvious inequality

$$\langle f|-\nabla^2|f\rangle \leq \langle f|-\nabla^2|f\rangle + \tfrac{1}{4}\langle f|-\nabla_R^2|f\rangle = \langle f|K|f\rangle, \quad \text{(B16)}$$

where K is defined in (B1). One can also show that

$$\langle\nabla^2 f|\nabla^2 f\rangle \leq \langle Kf|Kf\rangle. \quad \text{(B17)}$$

The substitution of the bounds (B16) and (B17) into (B15) gives

$$\langle f|\delta(\vec{r})|f\rangle \leq \frac{3}{2\pi}\langle Kf|Kf\rangle^{1/2}\langle f|K|f\rangle^{1/2} \quad \text{(B18)}$$

which differs from (B8) only by a factor of $\sqrt{2}$. Following the steps leading to (B12) one then finds an analogous result for ϵ_{12}:

$$\epsilon_{12} \leq \epsilon_{12}^{\max} \equiv \frac{1}{1-\eta_{\max}^2}(2A^{1/2}\tilde{I}_{12}^{1/2} + A + \eta_{\max}^2\tilde{I}_{12}), \quad \text{(B19)}$$

where $A \equiv C/\sqrt{2}$ and C is defined in (B10).

The error bounds (B12) and (B19) were evaluated for the case of the 1078-parameter $\tilde{\psi}$ developed by Pekeris,[3] with E_0 approximated by the corresponding $\tilde{E}_0$. Other sources[17,18] provided values for $\eta_{\max}^2$ and σ^2. These values are presented together with the results for $\epsilon_1^{\max}$ and $\epsilon_{12}^{\max}$ in Table II.

TABLE II. Upper bounds $\epsilon_1^{\max}$ and $\epsilon_{12}^{\max}$ for the error ϵ_1 and ϵ_{12} in $\tilde{I}_1$ and $\tilde{I}_{12}$, respectively, defined by Eqs. (B2) and (B3) of the text; also listed are the values of the quantities $\tilde{E}_0 = \langle\tilde{\psi}|H|\tilde{\psi}\rangle$, $\sigma^2 = \langle\tilde{\psi}|H^2|\tilde{\psi}\rangle - \tilde{E}_0^2$ and $\eta_{\max}^2$ [defined by Eq. (B5)] needed for the evaluation of the ϵ's via Eqs. (B12) and (B19).

$\epsilon_1^{\max}$ (a.u.)	$\epsilon_{12}^{\max}$ (a.u.)	$\tilde{E}_0$ (a.u.)	$\eta_{\max}^2$	σ^2 (a.u.)
0.0012	0.00025	−2.903 724 375 [a]	2×10^{-9} [b]	1.698×10^{-6} [c]

[a] See Ref. 3. [b] See Ref. 17. [c] See Ref. 18.

[1]For recent reviews of parity-violating effects in atomic physics see papers by G. Feinberg and P. G. H. Sandars, in Proceedings of the Ben Lee Memorial Conference, October, 1977, Batavia, Illinois (unpublished) and by L. Wilets, in Proceedings of Neutrinos-78, International Conference on Neutrino Physics and Neutrino Astrophysics, April 1978, Purdue, Indiana (unpublished).

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