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Parity-violating electric-dipole transitions in helium

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We study the parity-violating electric-dipole transitions $\gamma + 2\,{}^3S_1 \rightarrow 2\,{}^1S_0$ and $\gamma + 2\,{}^3P_0 \rightarrow 2\,{}^1P_1$ in He in order to gain some insight into the reliability of approximate calculations which have been carried out for similar transitions in many-electron atoms. The contributions of the nearest-lying states are computed with a variety of wave functions, including very simple product wave functions, Hartree-Fock functions, and Hylleraas-type wave functions with up to eighty-four parameters. We find that the values for the matrix elements of the parity-violating interaction which are given by the fairly simple wave functions can differ considerably from the values obtained from the very good wave functions, even when these simple wave functions give accurate values for energies and dipole matrix elements. An identity derived in a previous paper, which converts a delta-function matrix element to that of a global operator, is used to obtain alternative values for the matrix elements in question. It is found that use of this identity can substantially improve the results obtained with less accurate wave functions. We discuss the implications of our results for calculations of parity mixing in many-electron atoms.

I. INTRODUCTION

The investigation of parity-violating effects in many-electron atoms continues to be of considerable interest.[1] From a theoretical point of view, the reliable calculation of such effects is made difficult by several factors. The first is of course that accurate many-electron bound-state wave functions $\psi = \psi(\vec{r}_1, \ldots, \vec{r}_Z)$ are not readily available. The second is that the parity-violating interactions are of very short range, involving operators proportional to $\delta(\vec{r}_i)$ or $\delta(\vec{r}_i - \vec{r}_j)$, and this would seem to require special accuracy of the ψ's in parts of configuration space where wave functions which have been obtained by a variational principle cannot be expected to be particularly reliable. The third is the fact that, depending on circumstances, the contributions from many intermediate states, including those in the continuum, may have to be taken into account. Finally, for large Z relativistic effects are important and must be treated carefully.

Because of these factors, the calculations in cases of practical interest have been carried out only with the use of approximations whose accuracy is difficult to assess. The only case in which essentially exact calculations can be carried out is that of the hydrogen atom. In the present paper we study the problem of parity mixing for the next simplest case, that of helium. Because relatively good wave functions are available, one may hope to be able to make fairly accurate calculations. In particular, we have chosen to study parity-violating $E1$ transitions between the $n=2$ levels in He:

$$\gamma + 2\,{}^3S_1 \rightarrow 2\,{}^1S_0\,, \tag{1.1}$$

$$\gamma + 2\,{}^3P_0 \rightarrow 2\,{}^1P_1\,. \tag{1.2}$$

Such transitions are unlikely to be observed in the near future. However, one can use the theoretical results to test various approximations which have been made for the heavy atoms and thus get some insight into their reliability. Since Z is small, the relativistic effects that are important in heavy atoms are negligible, and one can examine the influence of the other factors mentioned above separately.

In the dipole approximation and in the nonrelativistic limit, the matrix element for a transition such as (1.1) is given by $-eM_{fi}/(2\omega)^{1/2}$, where $\omega = k = W_f - W_i$ is the photon energy and[2]

$$M_{fi} = \omega \sum_n \frac{\langle \Psi_f | H_{\rm pv} | \Psi_n \rangle \langle \Psi_n | i\vec{\epsilon}\cdot\vec{r}_1 + i\vec{\epsilon}\cdot\vec{r}_2 | \Psi_i \rangle}{W_f - W_n} + \omega \sum_n \frac{\langle \Psi_f | i\vec{\epsilon}\cdot\vec{r}_1 + i\vec{\epsilon}\cdot\vec{r}_2 | \Psi_n \rangle \langle \Psi_n | H_{\rm pv} | \Psi_i \rangle}{W_i - W_n}\,. \tag{1.3}$$

Here

$$H_{\rm nr}\Psi_n = W_n \Psi_n\,, \tag{1.4}$$

with

$$H_{\mathrm{nr}} = \sum_{i=1}^{2} (\vec{p}_i^{\,2}/2m - Z\alpha/r_i) + \alpha/r_{12}\,, \qquad (1.5)$$

and H_{pv} is the nonrelativistic (nr) form of the parity-violating interaction. Although the electron-electron neutral current effects may be important in He, we do not consider them here because our purpose is comparison with the heavy atoms calculation where only the electron-nucleon weak interaction has been taken into account. Thus we take

$$H_{\mathrm{pv}} = \sum_{i=1}^{2} H_{\mathrm{pv}}(i)\,, \qquad (1.6\mathrm{a})$$

with

$$H_{\mathrm{pv}}(i) \equiv G_{\mathrm{eff}}(\vec{\sigma}_i \cdot \vec{p}_i\, \delta(\vec{r}_i) + \delta(\vec{r}_i)\vec{\sigma}_i \cdot \vec{p}_i)/2m\,, \qquad (1.6\mathrm{b})$$

and, for ^{4}He,

$$G_{\mathrm{eff}} \approx -4(G_F/\sqrt{2})\sin^2\theta_W \qquad (1.7)$$

in the Weinberg-Salam model, with θ_W the Weinberg angle.

In a recent paper,[3] we have exhibited several identities which transform the expectation value of δ-function operators between eigenfunctions of a Hamiltonian H into the expectation value of "distributed operators" which get contributions from all parts of configuration space. It was argued there that the transformed form ought to give more accurate values when only approximate wave functions are available. In support of this idea it was shown that the use of these identities leads to an increase in percent accuracy by an order of magnitude in the evaluation of some of the relativistic corrections to the ground state of helium with Hylleraas-type wave functions. These techniques have also been generalized to include scattering states with encouraging results.[4] As was shown in Ref. 3, for any two eigenfunctions Ψ_a and Ψ_b of (1.3), one has

$$\begin{aligned}\langle \Psi_a | \vec{\sigma}_1 \cdot \vec{p}_1 \delta(\vec{r}_1) + \delta(\vec{r}_1)\vec{\sigma}_1 \cdot \vec{p}_1 | \Psi_b \rangle /2m &= (i/4\pi)(W_a - W_b)\langle \Psi_a | \vec{\sigma}_1 \cdot \vec{r}_1/r_1^3 | \Psi_b \rangle \\ &\quad + (i/4\pi m)[\langle \vec{p}_1 \Psi_a | \cdot \vec{\sigma}_1 \times \vec{l}_1/r_1^3 | \Psi_b \rangle - \langle (\vec{\sigma}_1 \times \vec{l}_1/r_1^3)\Psi_a | \cdot \vec{p}_1 | \Psi_b \rangle]\,. \end{aligned} \qquad (1.8)$$

On substituting (1.8) into (1.3), we get an alternative expression M'_{fi} for M_{fi} [see Eq. (2.11) of Sec. II]. If we replace the wave functions in M_{fi} and M'_{fi} by approximate ones, we will obtain approximate values $\tilde{M}_{fi}$ and $\tilde{M}'_{fi}$ which will in general not coincide,

$$\tilde{M}_{fi} \neq \tilde{M}'_{fi}\,, \qquad (1.9)$$

and the comparison of these different values may give some insight into the reliability of either value. If these values differ substantially, it suggests that neither should be regarded as reliable.

In Sec. II, we specialize the formulas for M_{fi} and M'_{fi} to the case of the transitions (1.1) and (1.2). In Sec. III, we compute the relevant matrix elements for a variety of approximate wave functions $\tilde{\psi}$ ranging from simple product functions to 84-parameter Hylleraas-type wave functions. In the final Sec. IV we summarize the results and discuss the implications for calculations of parity mixing in more complicated atoms.

II. $E1$ TRANSITIONS BETWEEN 2S STATES AND BETWEEN 2P STATES: PRELIMINARIES

A. 2S states

Consider the transition (1.1),

$$\gamma + 2\,^3S_1 \to 2\,^1S_0\,.$$

We write the final state as

$$\Psi_f = \psi_f\, \chi_0^0\,, \qquad (2.1)$$

where $\psi_f = \psi_f(\vec{r}_1, \vec{r}_2)$ is the spatial wave function, symmetric in $\vec{r}_1$ and $\vec{r}_2$, and χ_0^0 is the spin wave function for total spin equal to zero. Similarly, we write

$$\Psi_i = \psi_i\, \chi_{m_i}^1\,, \qquad (2.2)$$

with ψ_i antisymmetric and $\chi_{m_i}^1$ a spin-1 wave function. The intermediate states Ψ_n in the transition matrix element M_{fi} (1.3) may be separated into states that are spatially symmetric, $\psi_n^+\chi_0^0$, and states that are spatially antisymmetric, $\psi_n^-\chi_{m_s}^1$. On use of the orthogonality of χ^1 and χ^0 one finds readily that M_{fi} may be written in the form

$$M_{fi} = 4\,\frac{\omega G_{\mathrm{eff}}}{m} \sum_{\alpha,\beta = x,y,z} \langle \chi_0^0 | \sigma_1^\alpha | \chi_{m_i}^1 \rangle \epsilon^\beta T_{fi}^{\alpha\beta}\,, \qquad (2.3\mathrm{a})$$

where

$$T_{fi}^{\alpha\beta} = \sum_n \left(\frac{\langle \psi_f | t_1^\alpha | \psi_n^- \rangle \langle \psi_n^- | i r_1^\beta | \psi_i \rangle}{W_f - W_n^-} + \frac{\langle \psi_f | i r_1^\beta | \psi_n^+ \rangle \langle \psi_n^+ | t_1^\alpha | \psi_i \rangle}{W_i - W_n^+} \right), \qquad (2.3\mathrm{b})$$

with

$$\vec{t}_i = [\vec{p}_i \delta(\vec{r}_i) + \delta(\vec{r}_i)\vec{p}_i]/2 \quad (i = 1, 2)\,. \qquad (2.3\mathrm{c})$$

Since the initial and final spatial states are spherically symmetric, we may write

$$T_{fi}^{\alpha\beta}=\delta^{\alpha\beta}T_{fi}\,, \tag{2.4a}$$

with, e.g.,

$$T_{fi}=T_{fi}^{zz}\,. \tag{2.4b}$$

With this simplification, (2.3a) becomes

$$M_{fi}=4(\omega G_{\text{eff}}/m)\langle\chi_0^0|\vec{\epsilon}\cdot\vec{\sigma}_1|\chi_{m_i}^1\rangle T_{fi}\,. \tag{2.5}$$

As mentioned in Sec. I, the identity (1.8) which relates the matrix element of $\vec{\sigma}_1\cdot\vec{t}_1$ to the matrix element of a global operator can be used to obtain an alternative expression for M_{fi} and hence for T_{fi}. It is convenient to use a shorthand notation by introducing a formal operator $\vec{D}_i$ $(i=1,2)$ defined indirectly by

$$\langle\Psi_c|\vec{D}_i|\Psi_d\rangle\equiv(i/4\pi)[-\langle\vec{p}_i\Psi_c|\times\vec{l}_i/r_i^3|\Psi_d\rangle$$
$$-\langle(\vec{l}_i/r_i^3)\Psi_c|\times\vec{p}_i|\Psi_d\rangle]\,, \tag{2.6a}$$

and, consistent with (2.6a),

$$\langle\Psi_a|\vec{\sigma}_i\cdot\vec{D}_i|\Psi_b\rangle=(i/4\pi)[\langle\vec{p}_i\Psi_a|\cdot\vec{\sigma}_i\times\vec{l}_i/r_i^3|\Psi_b\rangle$$
$$-\langle(\vec{\sigma}_i\times\vec{l}_i/r_1^3)\Psi_a|\cdot\vec{p}_i|\Psi_b\rangle]\,. \tag{2.6b}$$

Using the definition (2.6b), we see that (1.8) may be rewritten as

$$\langle\Psi_a|\vec{\sigma}_1\cdot\vec{t}_1|\Psi_b\rangle=i(m/4\pi)(W_a-W_b)\langle\Psi_a|\vec{\sigma}_1\cdot(\vec{r}_1/r_1^3)|\Psi_b\rangle$$
$$+\langle\Psi_a|\vec{\sigma}_1\cdot\vec{D}_1|\Psi_b\rangle\,. \tag{2.7}$$

The substitution of (2.7) into the original expression (1.3) for M_{fi} yields

$$M_{fi}=M'_{fi}+4i\frac{\omega G_{\text{eff}}}{m}\sum_n\left(\frac{m}{4\pi}\langle\Psi_f|\vec{\sigma}_1\cdot(\vec{r}_1/r_1^3)|\Psi_n\rangle\langle\Psi_n|i\vec{\epsilon}\cdot\vec{r}_1|\Psi_i\rangle-\frac{m}{4\pi}\langle\Psi_f|i\vec{\epsilon}\cdot\vec{r}_1|\Psi_n\rangle\langle\Psi_n|\vec{\sigma}_1\cdot(\vec{r}_1/r_1^3)|\Psi_i\rangle\right)\,, \tag{2.8}$$

where

$$M'_{fi}=4\frac{\omega G_{\text{eff}}}{m}\sum_n\left(\frac{\langle\Psi_f|\vec{\sigma}_1\cdot\vec{D}_1|\Psi_n\rangle\langle\Psi_n|i\vec{\epsilon}\cdot\vec{r}_1|\Psi_i\rangle}{W_f-W_n}\right.$$
$$\left.+\frac{\langle\Psi_f|i\vec{\epsilon}\cdot\vec{r}_1|\Psi_n\rangle\langle\Psi_n|\vec{\sigma}_1\cdot\vec{D}_1|\Psi_i\rangle}{W_i-W_n}\right)\,. \tag{2.9}$$

It is understood that the sum on n in all formulas excludes $n=i$ and $n=f$. Since the matrix elements vanish for these values of n, the sum in (2.8) can be extended to include them. Using completeness of the Ψ_n and the fact that

$$[\vec{\sigma}_1\cdot(\vec{r}_1/r_1^3),i\vec{\epsilon}\cdot\vec{r}_1]=0\,,$$

we see that the sum on n in (2.8) has the value zero and therefore

$$M_{fi}=M'_{fi}\,. \tag{2.10}$$

The form of M'_{fi} allows it to be reduced in the same manner as M_{fi} to

$$M'_{fi}=4(\omega G_{\text{eff}}/m)\langle\chi_0^0|\vec{\epsilon}\cdot\vec{\sigma}_1|\chi_{m_i}^1\rangle T'_{fi}\,, \tag{2.11a}$$

where

$$T'_{fi}=\sum_n\left(\frac{\langle\psi_f|D_1^z|\psi_n^-\rangle\langle\psi_n^-|iz_1|\psi_i\rangle}{W_f-W_n^-}\right.$$
$$\left.+\frac{\langle\psi_f|iz_1|\psi_n^+\rangle\langle\psi_n^+|D_1^z|\psi_i\rangle}{W_i-W_n^+}\right)\,. \tag{2.11b}$$

From (2.5), (2.11a), and (2.10), we infer that

$$T_{fi}=T'_{fi}\,. \tag{2.12}$$

Because of the energy denominators present in (2.3b) and (2.11b), the near-lying $2P$ states are expected to make a large contribution to the sum over states. We make their special status explicit by writing

$$T_{fi}=T_{fi}^{2P}+T_{fi}^{\text{rem}} \tag{2.13a}$$

and

$$T'_{fi}=T_{fi}'^{2P}+T_{fi}'^{\text{rem}}\,, \tag{2.13b}$$

where "rem" stands for the remainder. Here T_{fi}^{2P} denotes the contribution to T_{fi} from the $2P$ states $\psi_{2P,m_l}^{\pm}$, where m_l is the component of $\vec{L}=\vec{l}_1+\vec{l}_2$ along the z axis and $T_{fi}'^{2P}$ is similarly defined. Only $m_l=0$ states can give nonzero contributions to T_{fi}^{zz}, so that

$$T_{fi}^{2P}=\frac{\langle\psi_f|t_1^z|\psi_{2P,0}^-\rangle\langle\psi_{2P,0}^-|iz_1|\psi_i\rangle}{W_f-W_{2P}^-}$$
$$+\frac{\langle\psi_f|iz_1|\psi_{2P,0}^+\rangle\langle\psi_{2P,0}^+|t_1^z|\psi_i\rangle}{W_i-W_{2P}^+}\,. \tag{2.14}$$

An analogous expression holds for $T_{fi}'^{2P}$ with t_1^z replaced by D_1^z.

One should note that in general T_{fi}^{2P} and $T_{fi}'^{2P}$ are *not* equal. On use of the identity (2.7), we have

$$T_{fi}^{2P}=T_{fi}'^{2P}+\Delta\,, \tag{2.15a}$$

$$T_{fi}^{\text{rem}}=T_{fi}'^{\text{rem}}-\Delta\,, \tag{2.15b}$$

where

$$\Delta=m[\langle\psi_f|(iz_1/4\pi r_1^3)|\psi_{2P,0}^-\rangle\langle\psi_{2P,0}^-|iz_1|\psi_i\rangle$$
$$-\langle\psi_f|iz_1|\psi_{2P,0}^+\rangle\langle\psi_{2P,0}^+|(iz_1/4\pi r_1^3)|\psi_i\rangle]\,. \tag{2.16}$$

Therefore when approximate wave functions are used one should compare T_{fi}^{2P} with $T_{fi}'^{2P}+\Delta$. However, because there is no energy denominator in

(2.16), Δ is small compared to either T_{fi}^{2P} or $T_{fi}'^{2P}$, as we shall see.

For the purpose of later comparison of different wave functions it is convenient to introduce separate symbols for the matrix elements entering the calculation of T_{fi}^{2P}, $T_{fi}'^{2P}$, etc. Thus, we define, for $\psi_i=\psi_{2S}^-$ and $\psi_f=\psi_{2S}^+$,

$$O_\pm \equiv \langle \psi_{2P,0}^\pm | z_1 | \psi_{2S}^\pm \rangle , \tag{2.17}$$

$$P_\pm \equiv \langle \psi_{2P,0}^\mp | i t_1^z | \psi_{2S}^\pm \rangle , \tag{2.18}$$

$$P_\pm' \equiv \langle \psi_{2P,0}^\mp | i D_1^z | \psi_{2S}^\pm \rangle , \tag{2.19}$$

and

$$Q_\pm \equiv m(W_{2S}^\pm - W_{2P}^\mp)\langle \psi_{2P,0}^\mp | z_1/4\pi r_1^3 | \psi_{2S}^\pm \rangle . \tag{2.20}$$

Then (2.14) takes the form

$$T_{fi}^{2P} = -\frac{P_+^* O_-}{W_{2S}^+ - W_{2P}^-} + \frac{O_+^* P_-}{W_{2S}^- - W_{2P}^+} , \tag{2.21}$$

and $T_{fi}'^{2P}$ is given by

$$T_{fi}'^{2P} = -\frac{P_+'^* O_-}{W_{2S}^+ - W_{2P}^-} + \frac{O_+^* P_-'}{W_{2S}^- - W_{2P}^+} . \tag{2.22}$$

From (2.7) it follows that

$$P_\pm = P_\pm' + Q_\pm \tag{2.23}$$

and (2.16) takes the form

$$\Delta = -\frac{Q_+^* O_-}{W_{2S}^+ - W_{2P}^-} + \frac{O_+^* Q_-}{W_{2S}^- - W_{2P}^+} . \tag{2.24}$$

B. 2P states

In the approximation in which only the 2S states are kept as intermediate states, the amplitude for

$$\gamma + 2\,{}^3P_0 \rightarrow 2\,{}^1P_1$$

involves essentially the same matrix elements which occur in the amplitude for $\gamma + 2\,{}^3S_1 \rightarrow 2\,{}^1S_0$, although different combinations of these matrix elements appear. We shall therefore give only a brief discussion. The initial and final atomic state may be written in the form

$$\Psi_i = \frac{1}{\sqrt{3}} \sum_{m=-1}^{1} (-1)^{m+1} \psi_{2P,m}^- \chi_{-m}^1 , \tag{2.25}$$

$$\Psi_f = \psi_{2P,m_f}^+ \chi_0^0 . \tag{2.26}$$

On substitution of (2.25) and (2.26) into (1.3), we find that the analog of (2.25) is

$$M_{fi} = (4\omega G_{\text{eff}}/m)(-1)^{m_f+1} \epsilon_{-m_i} \mathcal{T}_{fi} , \tag{2.27}$$

where $\epsilon_\pm = \mp(\epsilon_x \pm i\epsilon_y)/\sqrt{2}$ and $\epsilon_0=\epsilon_z$ are the spherical components of $\vec{\epsilon}$. Here $\mathcal{T}_{fi}$ is defined by

$$\mathcal{T}_{fi} = -\sum_n \left[3\,{}_1\mathcal{T}_{fi}^{nS} + {}_2\mathcal{T}_{fi}^{nS} + 2\mathcal{T}_{fi}^{nP} + (\sqrt{15}/2)\,\mathcal{T}_{fi}^{nD}\right] , \tag{2.28}$$

with

$${}_1\mathcal{T}_{fi}^{nS} \equiv \frac{1}{\sqrt{3}} \frac{\langle \psi_{2P,0}^+ | t_1^z | \psi_{nS}^- \rangle \langle \psi_{nS}^- | i z_1 | \psi_{2P,0}^- \rangle}{W_{2P}^+ - W_n^-} , \tag{2.29a}$$

$${}_2\mathcal{T}_{fi}^{nS} \equiv \frac{1}{\sqrt{3}} \frac{\langle \psi_{2P,0}^+ | i z | \psi_{nS}^+ \rangle \langle \psi_{nS}^+ | t_1^z | \psi_{2P,0}^- \rangle}{W_{2P}^- - W_n^+} , \tag{2.29b}$$

representing the contributions of intermediate S states and [$r_1^+ = -(x_1+iy_1)/\sqrt{2}$, etc.]

$$\mathcal{T}_{fi}^{nP} \equiv \frac{1}{\sqrt{3}} \frac{\langle \psi_{2P,0}^+ | t_1^- | \rangle \langle \psi_{nP,1}^- | i r_1^+ | \psi_{2P,0}^- \rangle}{W_{2P}^+ - W_n^-} , \tag{2.29c}$$

$$\mathcal{T}_{fi}^{nD} \equiv \frac{1}{\sqrt{3}} \frac{\langle \psi_{2P,0}^+ | t_1^Z | \psi_{nD,0}^- \rangle \langle \psi_{nD,0}^- | i Z_1 | \psi_{2P,0}^- \rangle}{W_{2P}^+ - W_n^-} , \tag{2.29d}$$

those of P states and D states. We may write, in analogy with (2.13a),

$$\mathcal{T}_{fi} = \mathcal{T}_{fi}^{2S} + \mathcal{T}_{fi}^{\text{rem}} , \tag{2.30}$$

where $\mathcal{T}_{fi}^{2S}$ denotes the total contribution of the 2S states and $\mathcal{T}_{fi}^{\text{rem}}$ the remainder. From (2.28) and the definitions (2.17) and (2.18), we have

$$\begin{aligned}\mathcal{T}_{fi}^{2S} &= -(3\,{}_1\mathcal{T}_{fi}^{2S} + {}_2\mathcal{T}_{fi}^{2S}) \\ &= \frac{-1}{\sqrt{3}} \left(\frac{3P_- O_-^*}{W_{2P}^+ - W_{2S}^-} - \frac{O_+ P_+^*}{W_{2P}^- - W_{2S}^+} \right) .\end{aligned} \tag{2.31}$$

It follows that when only the nearest states are included the calculation of the $E1$ transition between the 2P states involves basically the same quantities encountered in the calculation for 2S states.

III. WAVE FUNCTIONS AND NUMERICAL RESULTS

We now turn to a study of the values $\tilde{O}_\pm$, $\tilde{P}_\pm$, and $\tilde{P}_\pm'$ obtained by substituting a variety of approximate wave functions $\tilde{\psi}$ for the exact ones entering the definitions (2.17)–(2.19). We shall consider five types of wave functions: (i) Simple product wave functions with effective charges determined by the variational principle, (ii) similar wave functions which are corrected for correlation by the inclusion of dipole distortion ("polarized orbitals"), (iii) Hartree-Fock wave functions, (iv) wave functions obtained from effective central potentials with adjustable parameters and, finally, (v) Hylleraas-type variational wave functions with up to eighty-four linear parameters.

A. Simple-product wave functions

The general form of appropriately symmetrized product spatial wave functions for the $1s2s$ configuration is

$$\begin{aligned}\tilde{\psi}_{2S}^\pm = (N_\pm/\sqrt{2})\,[&\phi_{2s}^\pm(\vec{r}_1)\phi_{1s}^\pm(\vec{r}_2) \\ &\pm \phi_{2s}^\pm(\vec{r}_2)\phi_{1s}^\pm(\vec{r}_1)] ,\end{aligned} \tag{3.1a}$$

with $\tilde{\psi}^+_{2S}$ and $\tilde{\psi}^-_{2S}$ corresponding to the $2\,^1S_0$ and $2\,^3S_1$ states, respectively. The orbitals have the form

$$\phi^{\pm}_{ns}(\vec{r}) = R^{\pm}_{n0}(r)/(4\pi)^{1/2} \quad (n=1,2)\,, \tag{3.1b}$$

and the $N_\pm$ are normalization factors defined by

$$N_\pm = (1 \pm \langle R^{\pm}_{20} | R^{\pm}_{10}\rangle^2)^{-1/2}\,. \tag{3.1c}$$

For the $1s2p$ configuration we write, when $J_z = 0$,

$$\tilde{\psi}^{\pm}_{2P} = (1/\sqrt{2})\,[\phi^{\pm}_{2p,0}(\vec{r}_1)\phi'^{\pm}_{1s}(\vec{r}_2) \pm \phi^{\pm}_{2p,0}(\vec{r}_2)\phi'^{\pm}_{1s}(\vec{r}_1)]\,, \tag{3.2a}$$

with $\tilde{\psi}^+_{2P}$ and $\tilde{\psi}^-_{2P}$ associated with the $2\,^1P_1$ and $2\,^3P_0$ states, respectively, and $\phi^{\pm}_{2p,0}(\vec{r}_1)$ an $l=1$ orbital with $m_l = 0$. Thus we write

$$\phi^{\pm}_{2p,0}(\vec{r}) = R^{\pm}_{21}(r)Y^0_1(\hat{r}), \quad \phi'^{\pm}_{1s}(\vec{r}) = \mathcal{R}_{10}(r)/(4\pi)^{1/2}\,, \tag{3.2b}$$

with $Y^0_1(\hat{r}) = (3/4\pi)^{1/2}\cos\theta$. We have used another symbol for the "core wave function" $\phi'^{\pm}_{1s}(\vec{r})$ entering (3.2) because it may differ from the analogous function $\phi^{\pm}_{1s}(\vec{r})$ in (3.1).

When (3.1) and (3.2) are used to approximate the ψ's in Eqs. (2.17)–(2.19) one finds, after carrying out the angular integrations, that the corresponding approximate values of the matrix elements are given by

$$\tilde{\mathcal{O}}_\pm = (N_\pm/2\sqrt{3})\,(\langle R^{\pm}_{21}|r|R^{\pm}_{20}\rangle\langle \mathcal{R}^{\pm}_{10}|R^{\pm}_{10}\rangle \pm \langle R^{\pm}_{21}|r|R^{\pm}_{10}\rangle\langle \mathcal{R}^{\pm}_{10}|R^{\pm}_{20}\rangle)\,, \tag{3.3}$$

$$\tilde{P}_\pm = -\frac{\sqrt{3}\,N_\pm}{16\pi}\,\frac{dR^{\mp}_{21}(0)}{dr}\,[R^{\pm}_{20}(0)\langle \mathcal{R}^{\mp}_{10}|R^{\pm}_{10}\rangle \pm R_{10}(0)\langle \mathcal{R}^{\mp}_{10}|R^{\pm}_{20}\rangle]\,, \tag{3.4}$$

$$\tilde{P}'_\pm = \frac{N_\pm}{4\pi\sqrt{3}}\,[\langle R^{\mp}_{21}|\frac{1}{r^3}\frac{d}{dr}|R^{\pm}_{20}\rangle\langle \mathcal{R}^{\mp}_{10}|R^{\pm}_{10}\rangle \pm \langle R^{\mp}_{21}|\frac{1}{r^3}\frac{d}{dr}|R^{\pm}_{10}\rangle\langle \mathcal{R}^{\mp}_{10}|R^{\pm}_{20}\rangle]\,, \tag{3.5}$$

with a similar equation for $\tilde{Q}_\pm$ obtained from (2.20).

The notation has so far been sufficiently general to be applicable to any kind of product wave functions, including Hartree-Fock functions to be studied in Sec. III C. Here we specialize to the simplest kind of exponential forms for the radial function which are consistent with the nature of the configurations and, in the case of the $2\,^1S_0$ state, with the requirement of orthogonality to the $1\,^1S_0$ ground state.

For the $2P$ states we use the radial functions determined by Eckart,[5] i.e., purely hydrogenic-type orbitals (atomic units are used henceforth)

$$R^{\pm}_{21}(r) = [(Z'^{\pm}_0)^{3/2}/\sqrt{24}]\,e^{-Z'^{\pm}_0 r/2}(Z'^{\pm}_0 r)\,,$$
$$\mathcal{R}^{\pm}_{10}(r) = 2(Z'^{\pm}_i)^{3/2}\,e^{-Z'^{\pm}_i r}\,, \tag{3.6}$$

where Z'_0 and Z'_i denote the effective charges seen by the outer and inner electrons, respectively, in the $1s2p$ configuration, as determined by the variational principle. For the $2S$ states we write

$$R^{\pm}_{20}(r) = Z_0^{3/2}\,e^{-Z^{\pm}_0 r/2}(c^{\pm}_0 + c^{\pm}_1 Z_0 r)\,,$$
$$R^{\pm}_{10}(r) = 2(Z^{\pm}_i)^{3/2}\,e^{-Z^{\pm}_i r}\,. \tag{3.7}$$

For the $2\,^3S_1$ state, the effective charges have been determined by Eckart[5] with the c_j fixed at the values corresponding to a purely hydrogenic-type orbital $R^-_{20}(r)$, i.e., with $c^-_0 = 1$, $c^-_1 = -0.5$. For the $2\,^1S_0$ we have taken the effective charges Z^+_0 and Z^+_i to be those determined by Hylleraas and Undheim[6] with a Hylleraas-type wave function involving six linear parameters. With these choices for the S-state effective charges we determined the linear parameters $c^{\pm}_0$ and $c^{\pm}_1$ in (3.7) by applying the variational principle and choosing the higher root of the secular determinant in the case of the $\tilde{\psi}^+_{2S}$ wave function.

The effective charges and associated energies are given in Table I. The linear parameters for the $2S$ states were found to be

$$c^+_0 = 0.794, \quad c^+_1 = -0.464, \quad c^-_0 = 0.734, \quad c^-_1 = -0.452\,. \tag{3.8}$$

Note that the ratios $c^+_1/c^+_0 = -0.58$ and $c^-_1/c^-_0 = -0.62$ both differ appreciably from the hydrogenic value of -0.50. With the forms (3.7) and (3.8) for the radial wave functions, the quantities appearing on the right-hand sides in Eqs. (3.3)–(3.5) may be evaluated analytically. The numerical results obtained for $\tilde{O}_\pm$, $\tilde{\mathcal{P}}_\pm$, and $\tilde{\mathcal{P}}'_\pm + \tilde{Q}_\pm$ are shown in the first row of Table II. The quantity $\tilde{Q}_\pm$ is very small compared to $\tilde{P}'_\pm$ of order 10^{-3} $\tilde{\mathcal{P}}'_\pm$, so that we do not tabulate it separately.

B. Polarized orbitals

As an alternative to the simple-product wave functions considered above which still allows

TABLE I. Effective charges and variational energy values for the simple-product functions defined by Eqs. (3.1), (3.2), (3.6), and (3.7) of the text. All numbers, except for the S-state energies are from Refs. 5 and 6.

State	Wave-function symbol	Effective charge inner	Effective charge outer	Energy (a.u.)
$2\,^1S_0$	$\tilde{\psi}^+_{2S}$	$Z^+_i = 2.08$	$Z^+_0 = 1.21$	−2.1377
$2\,^3S_1$	$\tilde{\psi}^-_{2S}$	$Z^-_i = 2.01$	$Z^-_0 = 1.53$	−2.1698
$2\,^1P_1$	$\tilde{\psi}^+_{2P}$	$Z'^+_i = 2.00$	$Z'^+_0 = 0.97$	−2.1225
$2\,^3P_0$	$\tilde{\psi}^-_{2P}$	$Z'^-_i = 1.99$	$Z'^-_0 = 1.09$	−2.1310

TABLE II. Values of matrix elements defined by Eqs. (2.17)–(2.20) of the text, obtained from a variety of approximate wave functions for the $2S$ and $2P$ states of helium.

Type of wave function	$\tilde{O}_+$	$\tilde{P}_+(10^2)$	$\tilde{P}'_+ + \tilde{Q}_+(10^2)$	$\tilde{O}_-$	$\tilde{P}_-(10^2)$	$\tilde{P}'_- + \tilde{Q}_-(10^2)$
Simple product	−1.41	−1.11	−1.19	−1.16	−0.684	−0.819
Polarized orbital	−1.45	−1.49		−1.54	+0.540	
Hartree-Fock	−1.14	−1.68	−1.56	−1.28	−0.721	−0.827
Parametric potential	−1.40	−2.80	−2.91	−1.23	−0.809	−0.880
84-parameter Hylleraas	−1.46	−1.35	−1.35	−1.27	−1.04	−1.06

calculations in closed form but includes some effect of electron-electron correlation (beyond that provided by the Pauli principle) we consider wave functions obtained by the method of polarized orbitals.[7] In this method, a product wave function is modified by the inclusion of distortion of the inner electron wave function by the adiabatic electrostatic field provided by the outer electron. If for simplicity we assume that the outer electron sees a unit charge (full screening by the inner electron) the wave functions describing a $(1s, nl)$ configuration are

$$\Phi^{\pm}_{1s,nl} = (N^{\pm}/\sqrt{2})[\phi^{Z=1}_{nlm}(\vec{r}_1)\phi^{Z=2}_{1s}(\vec{r}_2) \pm (\vec{r}_1 \leftrightarrow \vec{r}_2)]. \quad (3.9)$$

The polarized-orbital $\Phi^{\text{pol}\pm}_{nlm}$ associated with (3.9) is constructed by replacing $\phi_{1s}(\vec{r}_2)$ by a function $\phi^{\text{pol}}_{1s}(\vec{r}_2; \vec{r}_1)$ obtained by solving the Schrödinger equation for electron "2" moving in the potential $V = -2r_2^{-1} + r_{12}^{-1}$, with $\vec{r}_1$ fixed. In the dipole approximation, one finds that, with distortion neglected for $r_1 < r_2$,[7]

$$\phi^{\text{pol}}_{1s}(\vec{r}_2; \vec{r}_1) = \phi^{Z=2}_{1s}(\vec{r}_2) - [\theta(r_1 - r_2)/\sqrt{2\pi}\, r_1^2]r_1(1 + r_2)\, e^{-2r_2}\hat{r}_1 \cdot \hat{r}_2 . \quad (3.10)$$

Then

$$\Phi^{\text{pol}\pm}_{210} = (N_{\pm}/\sqrt{2})\,[\phi^{Z=1}_{210}(\vec{r}_1)\,\phi^{\text{pol}}_{1s}(\vec{r}_2; \vec{r}_1) \pm \phi^{Z=1}_{210}(\vec{r}_2)\,\phi^{\text{pol}}_{1s}(\vec{r}_1; \vec{r}_2)]. \quad (3.11)$$

Taking

$$\tilde{\psi}^{\pm}_{2S} = \Phi^{\text{pol}\pm}_{200}, \quad \tilde{\psi}^{\pm}_{2P} = \Phi^{\text{pol}\pm}_{210}, \quad (3.12)$$

we get the values for $\tilde{O}^{\pm}$, etc., shown in the second row of Table II.

It is instructive to compare, *enpassant*, the values of the matrix elements obtained from the $\Phi^{\pm}_{1s,nl}$, which contain screening only very crudely, with the values from the $\Phi^{\text{pol}\pm}_{2lm}$ and from the wave functions of the preceding section. We find $O_+ = -1.45$, $O_- = -1.55$ which are close to the values given in the second line of Table II, but

$$\tilde{P}_+ = -1.29 \times 10^{-2}, \quad \tilde{P}_- = +0.32 \times 10^{-2}. \quad (3.13)$$

Thus the rough inclusion of correlation via adiabatic dipole distortion of these very crude wave functions has an appreciable (but not favorable) effect on the matrix elements P_+ and P_-.[8]

C. Hartree-Fock wave functions

The problem of obtaining Hartree-Fock (HF) wave functions for the low-lying excited state of He (and two-electron ions) has been discussed extensively by Cohen and Kelly.[9] These authors stress the importance of assuring that the HF wave function associated with the $2\,^1S_0$ state be orthogonal to the HF wave function for the ground state in obtaining a reasonable result for the energy of the $2\,^1S_0$ state. In the "frozen-core approximation" the S-state and P-state wave functions are written in the form

$$\Phi^{\pm}_S = (N^{\pm}/\sqrt{2})[R^{\pm}_S(r_1)R_c(r_2) \pm R^{\pm}_S(r_2)R_c(r_1)](1/4\pi), \quad (3.14)$$

$$\Phi^{\pm}_P = (1/\sqrt{2})[R^{\pm}_P(r_1)Y^0_1(\hat{r}_1)R_c(r_2) \pm R^{\pm}_P(r_2)Y^0_1(\hat{r}_1)R_c(r_1)](1/\sqrt{4\pi}), \quad (3.15)$$

with the core wave function $R_c(r)$ fixed to be that of the ground state of the He$^+$ ion,

$$R_c(r) = R^{Z=2}_{10}(r) = 4\sqrt{2}\,e^{-2r}. \quad (3.16)$$

The HF equation for $R^{\pm}_S(r)$ is then solved for the lowest two eigenvalues ϵ^+_{1s}, ϵ^+_{2s} and the associated orbitals $R^+_{1s}(r)$ and $R^+_{2s}(r)$. Although $\langle R^+_{2s}|R^+_{1s}\rangle \neq 0$, the associated two-particle wave functions $\tilde{\psi}^+_{1S}$ and $\tilde{\psi}^+_{2S}$ *are* orthogonal. For the $2\,^3S_1$, $2\,^3P_1$, and $2\,^1P_0$ states it suffices to find the lowest eigenvalue ϵ^-_{2S}, ϵ^-_{2P}, and ϵ^+_{2P} and the associated orbitals R^-_{2s}, R^-_{2p}, and R^+_{2p}, respectively. Because there is only one core wave function, the formulas (3.3), (3.4), and (3.5) simplify to

$$\tilde{O}_{\pm} = (N_{\pm}/2\sqrt{3})(\langle R^{\pm}_{2p}|r|R^{\pm}_{2s}\rangle \pm \langle R^{\pm}_{2p}|r|R_c\rangle I_{\pm}), \quad (3.17)$$

$$\tilde{P}_{\pm} = (-\sqrt{3}/16\pi)N_{\pm}\frac{dR^{\mp}_{2p}(0)}{dr}[R^{\pm}_{2s}(0) \pm R_c(0)I_{\pm}], \quad (3.18)$$

$$\tilde{P}'_{\pm} = \frac{N_{\pm}}{4\pi\sqrt{3}}\left(\left\langle R^{\mp}_{2p}\left|\frac{1}{r^3}\frac{d}{dr}\right|R^{\pm}_{2s}\right\rangle \pm \left\langle R^{\mp}_{2p}\left|\frac{1}{r^3}\frac{d}{dr_1}\right|R_c\right\rangle I_{\pm}\right), \tag{3.19}$$

where

$$I_{\pm} \equiv \langle R_c | R^{\pm}_{2s}\rangle \tag{3.20a}$$

is the overlap of the core with the $2s$ orbitals, and

$$N_{\pm} = (1 \pm I^2_{\pm})^{-1/2}. \tag{3.20b}$$

After numerical computation of the radial orbitals we find that

$$I_+ = 0.0818, \quad I_- = 5\times 10^{-6}, \tag{3.21}$$

$$\begin{aligned} &\langle R^-_{2p}|r|R^+_{2s}\rangle = -3.98, \quad \langle R^+_{2p}|r|R_c\rangle = 0.265, \\ &\langle R^-_{2p}|r|R^-_{2s}\rangle = -4.45, \quad \langle R^-_{2p}|r|R_c\rangle = 0.333, \end{aligned} \tag{3.22}$$

and

$$\begin{aligned} &dR^-_{2p}(0)/dr = 0.392, \quad R^+_{2S}(0) = 0.788, \\ &dR^+_{2p}(0)/dr = 0.201, \quad R^-_{2S}(0) = 1.042. \end{aligned} \tag{3.23}$$

On use of Eqs. (3.21)–(3.23) in Eqs. (3.17)–(3.19) we get the values of $\tilde{O}_{\pm}$, etc., shown in the third line of Table II.

It should be noted that the value of I_- has no direct physical significance because Φ^-_S is invariant under a change

$$R^-_S \to N(R^-_S + \beta R_c), \tag{3.24}$$

where N is a normalization constant. Correspondingly, to any solution R^-_S of the HF equation obtained from Φ^-_S there can always be added a piece proportional to R_c. Thus, one can require that

$$\langle R^-_{2s}|R_c\rangle = 0. \tag{3.25}$$

The small value of I_- [Eq. (3.21)] is just a reflection of this requirement; i.e., I_- is zero within the errors associated with numerical solutions. [As a check, note that if we make the replacement (3.24) inside the square brackets in (3.18) and in Eq. (3.20) the result for $\tilde{P}_{\pm}$ is unchanged.]

D. Wave functions from parametric central-field potentials

An alternative scheme to the HF approach in the many-body case has been used, e.g., by Neuffer and Commins,[10] to generate wave functions for one-electron excitation states in Cs and Tl. In this approach, one-electron wave functions are determined by solving a Dirac equation with a potential $V(r)$ which has the right asymptotic behavior for $r\to\infty$ ($V\sim 1/r$), and for $r\to 0$ ($V\sim -Z/r$), and which involves some adjustable parameters. These are fixed by requiring agreement with experimentally observed binding energies for one or more of the lowest-lying states. It is instructive to see how this works in the case of He. Following Ref. 9, we use the Tietz potential (a.u.):

$$V(r;\eta) = \frac{-1}{r}\left(\frac{Z-1}{(1+\eta r)^2} + 1\right). \tag{3.26}$$

Because the outer electron in low-lying singlet states sees rather a different potential than in triplet states, it is not feasible to use a single potential as in the case of Cs. Rather we write, for $Z=2$,

$$V_{\pm} = V(r;\eta_{\pm}) = \frac{-1}{r}\left(\frac{1}{(1+\eta_{\pm}r)^2} + 1\right), \tag{3.27a}$$

with $V_+(r)$ and $V_-(r)$ the effective potentials for the singlet and triplet states, respectively. We then require that

$$(-\tfrac{1}{2}\vec{\nabla}^2 + V_{\pm})R^{\pm}(r) = \epsilon^{\pm}_{2s}R^{\pm}(r), \tag{3.27b}$$

where $\epsilon^+_{2s} = -0.146$ and $\epsilon^-_{2s} = -0.175$ are the binding energies of the $2\,{}^1S$ and $2\,{}^3S$ states, respectively, with $R^{\pm}(r)$ an orbital with one node. We find

$$\eta_+ = 2.595, \quad \eta_- = 0.975. \tag{3.27c}$$

The values of the ϵ's for the $2\,{}^1P$ and $2\,{}^3P$ states then turn out to be

$$\bar{\epsilon}^+_{2p} = -0.129, \quad \bar{\epsilon}^-_{2p} = -0.146, \tag{3.28}$$

within 10% or better of the correct values $\epsilon^+_{2p} = -0.124$ and $\epsilon^-_{2p} = -0.133$. The values $\tilde{O}_{\pm}$, $\tilde{P}_{\pm}$, and $\tilde{P}'_{\pm} + \tilde{Q}_{\pm}$ obtained from the wave functions generated in this way are shown in the fourth line of Table II.

E. Many-parameter Hylleraas-type functions

As is well known, for the low-lying bound states of helium it is feasible to obtain accurate two-electron wave functions by using Hylleraas-type expansions. We denote a wave function with N linear parameters by ψ^N, and write

$$\begin{aligned} \psi^{N\pm}_{2S} &= g^{\pm}_N(r_1,r_2,r_{12}) \pm g^{\pm}_N(r_2,r_1,r_{12}), \\ \psi^{N\pm}_{2P} &= f^{\pm}_N(r_1,r_2,r_{12})\cos\theta_1 \pm f_N(r_2,r_1,r_{12})\cos\theta_2, \end{aligned} \tag{3.29}$$

with

$$\begin{aligned} g^{\pm}_N(r_1,r_2,r_{12}) &= e^{-\alpha_{\pm}r_1}e^{-\beta_{\pm}r_2}\sum_{ijk}B^{\pm}_{ijk}(N)r_1^i r_2^j r_{12}^k, \\ f^{\pm}_N(r_1,r_2,r_{12}) &= e^{-\gamma_{\pm}r_1}e^{-\delta_{\pm}r_2}\sum_{ijk}C^{\pm}_{ijk}(N)r_1^i r_2^j r_{12}^k. \end{aligned} \tag{3.30}$$

We restrict i, j, and k to be non-negative integers and require that, for r_1 small, $f^{\pm}_N \sim r_1$, so that $C^{\pm}_{0jk} = 0$. We will consider only choices of N corresponding to "Pekeris shells," so that all multinomials $r_1^i r_2^j r_{12}^k$ of the same degree $\omega = i+j+k$ occur, if any one of degree ω occurs. For $\omega_{\max}$

$=1, 2, \ldots, 6$ this gives $N=4$, 10, 20, 35, 56, and 84. For $N=4$ and 10 we use the variational principle for fixed starting values of the nonlinear parameters $\alpha_\pm, \beta_\pm, \ldots, \delta_\pm$ (for some of these we used the effective charges of Sec. III A) to determine the linear parameters B_{ijk} and C_{ijk}, and then vary the nonlinear parameters to lower the energy still further. A quick improvement can be obtained by rescaling, $r \rightarrow kr$. For $N>10$, we have used the nonlinear parameters found for $N=10$. It should be noted that for large enough N, the result for the energy will not be sensitive to the choice of the nonlinear parameters. The final values[11] used were, for $N=4$,

$$\begin{aligned} &\alpha_+=0.59\,, \quad \beta_+=2.01\,, \quad \gamma_+=0.60\,, \quad \delta_+=2.00\,, \\ &\alpha_-=0.73\,, \quad \beta_-=1.87\,, \quad \gamma_-=0.55\,, \quad \delta_-=2.02\,, \end{aligned} \tag{3.31}$$

and, for $N=10$,

$$\begin{aligned} &\alpha_+=0.61\,, \quad \beta_+=2.08\,, \quad \gamma_+=0.60\,, \quad \delta_+=2.00\,, \\ &\alpha_-=0.70\,, \quad \beta_-=1.80\,, \quad \gamma_-=0.70\,, \quad \delta_-=2.00\,. \end{aligned} \tag{3.32}$$

The energies are shown in Table III. The corresponding wave functions were used to compute approximate values of $\tilde{O}_\pm$, etc., with the results shown in Table IV.

Examination of Table IV shows that the variation of these values for large N is small. The values obtained for $N=84$ are probably within a few percent of the exact values and we shall use them as a standard for comparisons. The large error in the values of $\tilde{P}_+$ and $\tilde{P}_-$ found for $N=4$ is rather disturbing. Even for $N=10$, the value of P_+ is still in error by 30%. This shows that even wave functions which take correlation into account to a considerable extent may give rise to large errors in matrix elements sensitive to special regions in coordinate space, such as the origin. It should be noted that the values of $\tilde{P}'_\pm$ converge more rapidly to the final values than do the $\tilde{P}_\pm$, which provides encouragement for the use of the identity (1.8) in future calculations.

TABLE III. Variational energy values from N-term Hylleraas-type wave functions for the $2S$ and $2P$ states of helium, described by Eqs. (3.29) and (3.30) of the text.

N	$W^+_{2S}(N)$	$W^-_{2S}(N)$	$W^+_{2P}(N)$	$W^-_{2P}(N)$
4	−2.143 35	−2.173 22	−2.123 08	−2.131 78
10	−2.144 96	−2.175 20	−2.123 59	−2.133 02
20	−2.145 65	−2.175 23	−2.123 76	−2.133 11
35	−2.145 85	−2.175 23	−2.123 81	−2.133 16
56	−2.145 92	−2.175 23	−2.123 83	−2.133 16
84	−2.145 96	−2.175 23	−2.123 84	−2.133 17

F. Results for the T_{fi}

From Tables II and III we can readily compute the values of T^{2P}_{fi} and $\mathcal{T}^{2S}_{fi}$, the contributions of the near-lying states to the invariants T_{fi} and $\mathcal{T}_{fi}$ defined by Eqs. (2.5) and (2.27), for the transitions (1.1) and (1.2), respectively. Using Eqs. (2.21), (2.22), and (2.31), and its analog for $\mathcal{T}'^{2S}_{fi}$, obtained by replacing $P_\pm$ by $P'_\pm$ in (2.31), we find the results shown in Table V. We have used the best-known theoretical values for the energies $W^\pm_{2S}$ and $W^\pm_{2P}$ in the energy denominators appearing in the definitions of T^{2P}_{fi}, $\mathcal{T}^{2P}_{fi}$, etc., viz.,[12]

$$\begin{aligned} &W^+_{2S}=-2.145\,973\,3\,, \quad W^-_{2S}=-2.175\,229\,4\,, \\ &W^+_{2P}=-2.123\,843\,1\,, \quad W^-_{2P}=-2.133\,164\,2\,. \end{aligned}$$

These numbers give energy differences which, for practical purposes, coincide with the experimental values. An alternative calculation of the T_{fi} would utilize the energies associated with the wave functions used in computing the matrix elements in the numerators. However, we wished to follow as much as possible the many-body calculations, in which experimental energy differences are used whenever possible.

A discussion of the results exhibited in Tables II, IV, and V is given in the following section.

IV. DISCUSSION

A. Analysis of numerical results

As can be seen from Table IV, the matrix elements $\tilde{O}_\pm$ and $\tilde{P}_\pm$ obtained from the N-term Hylleraas-type wave functions converge towards stable values for large N. The $N=84$ values can thus be taken as standards for measuring the accuracy obtained with other wave functions. Since the Hartree-Fock (HF) and parametric-potential (pp) type of wave functions have been used in the calculations for many-electron atoms, we focus on these. Examination of Table II shows that the dipole matrix elements $\tilde{O}_\pm$ given by wave functions without correlation are for the most part within 10% or so of the correct values. It may be worth noting that the HF value for O_+ is in error by more than 20% while the pp values for both O_+ and O_- are within 5% of the correct values. However, neither the HF nor the pp type of wave functions gives good results for the weak-interaction matrix elements P_+ and P_-. The very large error in the pp value for P_+ is probably associated with the fact that the "real" potential seen by the p-wave electron in the $2\,^3P$ state is not as attractive as that given by using the value of η_- determined from the $2\,^3S$ state; in fact a much better value for P_+ would be obtained if for the $2\,^3P$ state one used $\eta_-=\infty$, i.e., full screening by the inner electron.

TABLE IV. Values of matrix elements defined by Eqs. (2.17)–(2.20) of the text, obtained from N-term Hylleraas-type wave functions for the $2S$ and $2P$ states of helium.

N	$\tilde{O}_+$	$\tilde{P}_+(10^2)$	$(\tilde{P}'_+ + \tilde{Q}_+)(10^2)$	$\tilde{O}_-$	$\tilde{P}_-(10^2)$	$(\tilde{P}'_- + \tilde{Q}_-)(10^2)$
4	−1.361	+0.28	−0.28	−1.211	−0.39	−0.66
10	−1.455	−0.92	−1.17	−1.263	−0.89	−0.94
20	−1.459	−1.32	−1.33	−1.266	−0.96	−1.01
35	−1.459	−1.37	−1.35	−1.266	−0.99	−1.04
56	−1.458	−1.34	−1.35	−1.266	−1.03	−1.05
84	−1.456	−1.35	−1.35	−1.266	−1.04	−1.06

Of course, such a procedure would not be in the spirit of a parametric-potential approach. It may be that the low-lying states of He are relatively unsuitable for this approach because of the importance of exchange effects.

Returning to Table IV, we note that, as already remarked in Sec. III, inclusion of correlation in the wave function does not guarantee that the resulting matrix elements will be accurate, especially for P_+ and P_-. Thus, although the ten-term Hylleraas-type wave functions give very good values for O_+ and O_-, the value for P_- is in error by 15% and that for P_+ by more than 30%. In fact, the value for P_+ given by the simple product wave functions is more accurate than that given by the ten-term Hylleraas-type wave function. Furthermore, the values of P_+ and P_- for $N=4$ are quite bad, with $\tilde{P}_+$ even having the wrong sign. Although these aspects of the results given by the correlated wave functions with $N \leqslant 10$ may well be numerical accidents, not characteristic of the general situation, it should give one pause in assessing the reliability of calculations which have been carried out for atoms with many electrons.

TABLE V. Contributions T_{fi}^{2P} and $\mathcal{T}_{fi}^{2S}$ of the near-lying P states and S states to the invariant amplitudes describing transitions between the $2S$ states and between the $2P$ states of He, respectively, for a variety of wave functions. The primed quantities are obtained by use of the identity (1.8).

Type of wave function	T_{fi}^{2P}	$T_{fi}'^{2P}$	$\mathcal{T}_{fi}^{2S}$	$\mathcal{T}_{fi}'^{2S}$
Simple product	0.82	0.85	0.438	0.436
Polarized orbital	1.94		1.254	
Hartree-Fock	1.52	1.38	0.552	0.445
Parametric potential	2.45	2.53	1.434	1.474
N-term Hylleraas:				
$N=4$	−0.37	0.09	−0.331	−0.098
10	0.66	0.89	0.225	0.367
20	1.03	1.03	0.458	0.444
35	1.07	1.04	0.479	0.444
56	1.03	1.04	0.441	0.439
84	1.04	1.03	0.442	0.434

With regard to the use of the identity (1.8), Table IV shows that the $\tilde{P}'_\pm$ values converge more rapidly towards their final values than do the $\tilde{P}_\pm$ values. (Recall that $\tilde{Q}_\pm$ is very small.) For example, when $N=10$ the error in $\tilde{P}'_+$ is only 13%, not 30%, and $\tilde{P}'_+$ for $N=4$ has at least the right sign. For large N, the primed and unprimed values become closely equal, as they eventually must if the wave functions are converging to the exact solutions. Table II shows that the primed values are also more accurate for other types of wave functions; the only exception is the value of $\tilde{P}'_\pm$ for the parametric-potential case, where both $\tilde{P}_+$ and $\tilde{P}'_+$ are in error by more than a factor of 2. Clearly, the identity cannot perform miracles: Although its use may yield a good result from fair wave functions, it cannot produce a good one from poor wave functions.

The approximate equality of $\tilde{P}_\pm$ and $\tilde{P}'_\pm$ is not in itself a sufficient condition for assuring that one is close to the correct value of $P_\pm$. To some extent this may be understood by considering the case where the approximate wave functions $\tilde{\Psi}$ employed happen to be eigenfunctions, with eigenvalues $\tilde{W}$, of an operator of the form

$$\tilde{H} = K_1 + K_2 + \tilde{U}_1 + \tilde{U}_2 , \tag{4.1}$$

where $\tilde{U}_1$ and $\tilde{U}_2$ are *local* potentials. For such wave functions the left- and right-hand sides of (1.8) are bound to give the same numerical results when the exact Ψ's are replaced by $\tilde{\Psi}$'s, and $W_a - W_b$ by $\tilde{W}_a - \tilde{W}_b$. In this respect the identity (1.8) is weaker than analogous identities for parity-conserving delta functions, in which the interaction potential enters explicitly.[13] Although the symmetrized product wave functions are not eigenfunctions of a Hamiltonian of the type (4.1), the unsymmetrized products from which they are constructed often are, as in the case of the simple product and pp type of wave functions.

The contributions of the near-lying states to the invariant transition amplitudes T_{fi} and $\mathcal{T}_{fi}$ describing the processes (1.1) and (1.2) are shown in Table V. Since the quantities T_{fi}^{2P} and $\mathcal{T}_{fi}^{2S}$ are calculated directly from the matrix elements $\tilde{O}_\pm$

and $\tilde{P}_\pm$ shown in Tables II and IV, the errors in these quantities, with the values obtained from the 84-term Hylleraas-type wave functions taken as a standard, largely reflect the errors in $\tilde{O}_\pm$ and $\tilde{P}_\pm$. In particular, we see from Table V that the HF value for T_{fi}^{2S} is in error by 50%, that for $\mathcal{T}_{fi}^{2P}$ by 25%, and that the pp values are off by more than a factor of 2. It is ironic that the best values for noncorrelated wave functions are given by the simple-product wave functions, based on effective charges. However this is certainly accidental because the matrix elements $\tilde{O}_\pm$ and $\tilde{P}_\pm$ obtained from these functions have appreciable errors, as Table II shows. The values shown for the Hylleraas-type wave functions again show more rapid convergence for the primed values and attest to the utility of the identity (1.8).

It would be interesting to know the contributions T_{fi}^{rem} and $\mathcal{T}_{fi}^{\text{rem}}$ of the remaining states to T_{fi} and $\mathcal{T}_{fi}$, respectively. A rough estimate of the contribution T_{fi}^{se} of singly excited states has been made. With hydrogenic-type product wave functions used to approximate the (ls, ns) states $(n \geqslant 3)$ one finds, on use of a Green's-function technique to carry out the sum over both bound and continuum states, that T_{fi}^{se} is less than 1% of T_{fi}^{2S}.[14] However, a similar calculation for the contribution of the $(ls; ns)$ states $(n \neq 2)$ to the $2\,{}^3P_0 \rightarrow 2\,{}^1P_1$ transition yields[14]

$$\mathcal{T}_{fi}^{\text{se}} \sim -0.21\,,$$

which is almost 50% of $\mathcal{T}_{fi}^{2S} = 0.44$ and of opposite sign. Thus it appears that for some transitions in He where there are near-lying states of opposite parity, significant contributions can come from states which are not particularly close in energy to either the initial or the final state.

B. Concluding remarks

In some of the calculations of parity mixing in many-electron atoms an additional check or constraint on the approximate wave functions was obtained by computing the part of the hyperfine splitting arising from the Fermi contact interaction

$$H_{\text{HF}}^{\text{cont}} = (\text{const}) \sum_{i=1}^{N} \vec{\sigma}_i \cdot \vec{S}_{\text{nuc}} \delta(\vec{r}_i)\,,$$

which tests the accuracy of the electron spin density at the origin. If we consider the case of ^{3}He we may carry out such a calculation for, e.g., the $2\,{}^3S_1$ state or the $2\,{}^1P_1$ state. Unfortunately, because we are then dealing with an unfilled inner shell, the splitting, which is proportional to $\langle \psi | \delta(\vec{r}_1) | \psi \rangle$ is then dominated by the contribution from the 1s electron. For example, the probability density for a 1s electron moving in a Coulomb field with $Z = 2$ to be at the origin is $32/8\pi \approx 1.27$. This may be compared with, e.g., the value of $\langle \delta(\vec{r}_1) \rangle = 1.32$ computed from the 84-term Hylleraas-type wave function for the $2\,{}^3S_1$ state defined in Sec. III. Indeed, most of the uncorrelated wave functions which we have considered in this paper give good results for the hyperfine splitting so that this splitting is not a useful diagnostic tool for the case at hand.

The substantial disagreement between accurate values for parity mixing matrix elements in helium and the results of Hartree-Fock or parametric-potential calculations suggest that similar calculations in heavy atoms may also be less accurate than supposed. While some quantities involving inner electrons can be expected to be calculated more accurately in heavy atoms than in helium by HF or pp methods, there is not much evidence that this is the case for quantities involving valence electrons, which are relevant to parity mixing.

As we have seen, the HF and pp wave functions in He give relatively inaccurate results for the contribution of the near-lying states to the transition amplitudes. It is plausible that similar inaccuracies will occur when such wave functions are used for heavy atoms. In heavy atoms there are usually appreciable contributions from states other than the nearest-lying ones, so that it is conceivable that the summation over states will alleviate these inaccuracies. However, we do not see any reason for this to occur. In that connection it is worth noting that estimates which have been made of T_{fi}^{se}, the contribution to T_{fi} of singly excited states with $n \geqslant 3$, were found to be quite sensitive to small changes in the form of the $n = 2$ S-state wave functions.[14] A similar sensitivity of these contributions to the initial and final wave functions may occur for heavy atoms.

We also note that the main inaccuracy in the matrix elements calculated with approximate wave functions in He occurs for the parity-mixing operator H_{pv} rather than for the $E1$ operator. This is relevant to calculations in which the matrix elements of H_{pv} are calculated approximately, while the $E1$ matrix elements are taken as far as possible, from experiment. A calculation procedure which gives accurate values for the hyperfine structure splittings in various states does not necessarily give equally accurate answers for parity-mixing matrix elements. The latter also involve derivatives of p-state wave functions at the origin, which do not enter into the hyperfine matrix elements. We know of no way of obtaining independent experimental information about these p-wave derivatives.

In conclusion, we believe that it remains to be shown that the methods that have been used to calculate parity mixing in heavy atoms are as accurate as has been suggested in the literature.[15]

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[1] For reviews see, e.g., G. Feinberg, in *Unification of Elementary Forces and Gauge Theories*, edited by D. Cline and F. Mills (Harwood, London, 1978), p. 117; P. G. H. Sandars, *ibid.*, p. 153.

[2] The justification for this formula for M_{fi}, involving the length form of the dipole operator, is more subtle than one might expect. See J. Hiller, J. Sucher, G. Feinberg, and B. Lynn, Ann. Phys. (N.Y.) (to be published).

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[7] For a review see R. J. Drachman and A. Temkin, in *Case Studies in Atomic Collision Physics*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1972), Vol. 2, p. 401. The method has been applied primarily to scattering problems.

[8] It should be emphasized that instead of $\phi_{2l0}^{Z=1}(\vec{r}_1)$ in (3.11) one should use a function $U_{2l}(r_1)Y_l^0(\hat{r}_1)$ with $U_{2l}(r_1)$ determined as the solution of an integro-differential equation (Ref. 7). The neglect of this distinction is a drastic additional approximation which may well account for the poor results obtained in $P_{\pm}$. Numerical solutions for $U_{2l}(r_1)$ have been obtained when the energy is positive [see I. H. Sloan, Proc. R. Soc. London 281, 151 (1964)] but are not available for the case at hand. It would be interesting to pursue this in a further study.

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[10] D. V. Neuffer and E. D. Commins, Phys. Rev. A 16, 1760 (1977).

[11] Four-term Hylleraas-type wave functions for the $2\,^3S$ and $2\,^3P$ states are given by J. Traub and H. M. Foley, Phys. Rev. 111, 1098 (1958); 116, 914 (1959). We have used the nonlinear parameters reported by these authors for the $2\,^3P$ state; our parameters for the $2\,^3S$ state differ slightly from theirs. Use of their $2\,^3S$ wave function gives essentially the same results as those obtained with ours.

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[13] For off-diagonal matrix elements of, e.g., $\delta(\vec{r}_1)$ between bound states, one can derive the relation, following the techniques of Ref. 3:

$$\langle \Psi_a | \delta(\vec{r}_1) | \Psi_b \rangle = \frac{m}{4\pi}(E_a - E_b)\left(\left\langle \Psi_a \middle| \frac{\partial \Psi_b}{\partial r_1} \right\rangle - \left\langle \frac{\partial \Psi_a}{\partial r_1} \middle| \psi_b \right\rangle\right) + \tfrac{1}{2}\left(\langle \Psi_a | D_1 | \Psi_b \rangle + \langle D_1 \Psi_a | \Psi_b \rangle\right),$$

where D_1 is a global operator, given in Ref. 3, which depends on the interaction potential.

[14] J. Hiller (unpublished).

[15] For a recent review and references see L. Wilets, in *Neutrinos–78* Proceedings of the International Conference For Neutrino Physics and Astrophysics, Purdue, 1978, edited by E. C. Fowler (Purdue University Press, W. Lafayette, Indiana, 1978), p. 437.