Pauli Approximation in Many-Electron Atoms*†

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The Pauli approximation for many-electron atoms is derived. This yields an unambiguous expression for the fine-structure splitting and other first-order relativistic corrections to the energy, using nonrelativistic wave functions. A formalism is developed for atoms, based on these results, which is suitable for the evaluation of the fine structure using multiconfiguration wave functions. Fine-structure splittings calculated from Hartree-Fock wave functions are presented for the ground states from He through Ar; the remaining energy corrections are also presented. Multiconfiguration results are presented for the lowest ^2D and ^2P states of N, accounting for about 80% of the discrepancy between Hartree-Fock values and experimental values.

I. INTRODUCTION

The Pauli approximation is the basis for most attempts to deal with relativistic effects in many-electron systems. In this approach, expressions are derived, with respect to the appropriate nonrelativistic wave function, which give the first-order corrections to the energy. Such expressions were found by Breit[1] for a two-electron system and appear, with a few modifications,[2-4] in their most familiar form as the terms H_1 through H_5 given by Bethe and Slapeter.[5] These terms give the fine structure and include, among others, spin-orbit, spin-spin, and spin-other-orbit couplings. They do not account for hyperfine structure or the effects of nuclear motion. The primary reason for the popularity of the Pauli approximation lies in its ease of application in comparison to more fully relativistic treatments: Only the nonrelativistic wave function need be dealt with, rather than the more complicated relativistic wave function.

In this paper we apply the Pauli approximation to the case of atoms. The formalism we develop here is of sufficient generality to apply to wave functions which are mixtures of configurations. We present expressions for all of the terms which contribute to the first-order relativistic correction to the energy.

We begin with a derivation of the Pauli approximation in Sec. II. The relativistic formalism from which we start is not entirely satisfactory: The terms for the electron-electron interactions are not Lorentz invariant, and higher-order quantum electrodynamical effects, such as those giving rise to the Lamb shift, are not included. It does, however, contain all the first-order relativistic effects, and therefore, suffices for a derivation of the Pauli approximation. Since our relativistic formalism treats an arbitrary number of electrons N, we obtain the Pauli approximation explicitly generalized to an N-electron system.

Along with such generality, our goal is derivation of the Pauli approximation characterized by sufficient rigor and attention to detail. In contrast to previous treatments,[1,6-10] we do not attempt to present the first-order relativistic correction to the energy in terms of an "equivalent Hamiltonian." Consequently, we obtain an expression which is entirely unambiguous and simple to evaluate.

In Sec. III the orbital integrals arising from the first-order relativistic energy corrections in atoms are presented. We outline the construction of multiconfiguration wave functions in Sec. IV and reduce the single-configuration matrix elements to simpler forms on the basis of their assumed symmetry properties. With these results in hand, we give expressions in terms of orbital radial integrals in Sec. V.

Numerical results, obtained by application of our formalism, are given in Sec. VI. These include results from Hartree-Fock wave functions for the ground states of He through Ar. We also give multiconfiguration calculations for the lowest nitrogen ^2D and ^2P states. These calculations yield substantial improvement in the computed fine-structure splittings in comparison to the Hartree-Fock results.

II. DERIVATION OF THE PAULI APPROXIMATION

The many-electron *Dirac Hamiltonian* $\mathfrak{D}$ for an N-electron system is, in atomic units,

$$\mathfrak{D}=\sum_{p} h_p + \tfrac{1}{2}\sum_{p}\sum_{q\neq p} 1/r_{pq} \ , \tag{1}$$

where the summations are from 1 to N, r_{pq} is the distance between the pth and qth electrons, and h_p is the Dirac Hamiltonian of the pth electron:

$$h_p = c^2\beta_p + c\vec{\alpha}_p\cdot\vec{\mathrm{p}}_p + V_p \ . \tag{2}$$

In Eq. (2) $\vec{p}$ is the momentum operator, V is the potential due to the nuclear and external fields, c is the speed of light, and $\vec{\alpha}$ and β are the Dirac matrices in conventional representation, namely

$$\vec{\alpha}=\begin{pmatrix}0 & \vec{\sigma}\\ \vec{\sigma} & 0\end{pmatrix}, \qquad \beta=\begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix}, \tag{3}$$

where $\vec{\sigma}$ has as its components the 2×2 Pauli matrices and I is the 2×2 unit matrix.

The Breit operator $\mathcal{B}$ for an N-electron system is

$$\mathcal{B}=\tfrac{1}{2}\sum_p \sum_{q\neq p} b_{pq} , \tag{4}$$

where

$$b_{pq}=-\tfrac{1}{2}[\vec{\alpha}_p\cdot\vec{\alpha}_q/r_{pq}+(\vec{\alpha}_p\cdot\vec{r}_{pq})(\vec{\alpha}_q\cdot\vec{r}_{pq})/r_{pq}^3] , \tag{5}$$

and the summations are again from 1 to N; we use $\vec{r}_{pq}$ for the quantity $(\vec{r}_p-\vec{r}_q)$. Roughly speaking, b_{pq} is the correction to the interaction term $1/r_{pq}$ due to first-order magnetic and retardation effects.[1,11]

The relativistic one-electron orbitals θ_i are four-component Dirac spinors which we take to form an orthonormal set:

$$\langle\theta_i|\theta_j\rangle=\delta_{ij} . \tag{6}$$

Note that the left-hand side of Eq. (6) involves a summation over four terms as well as integration over the space coordinates. It is also useful to write

$$\theta_i=\begin{pmatrix}\varphi_i\\ \chi_i\end{pmatrix} , \tag{7}$$

where φ_i and χ_i are two-component Pauli spinors: φ_i is the *large component* of θ_i, and χ_i is the *small component*.

From the set of orbitals θ_i we construct Slater determinants Θ_I:

$$\Theta_I=\{\theta_{i_1}\theta_{i_2}\ldots\theta_{i_N}\}=(N)^{-1/2}\begin{vmatrix}\theta_{i_1}(1) & \theta_{i_2}(1)\ldots\theta_{i_N}(1)\\ \theta_{i_1}(2) & \theta_{i_2}(2)\ldots\theta_{i_N}(2)\\ & \ldots\\ \theta_{i_1}(N) & \theta_{i_2}(N)\ldots\theta_{i_N}(N)\end{vmatrix} . \tag{8}$$

The index I indicates an *ordered* set of indices $i_1, i_2, \ldots, i_N$:

$$I=(i_1,i_2,\ldots,i_N) , \quad i_1<i_2<\cdots<i_N . \tag{9}$$

The ordering of the indices $i_1, i_2, \ldots, i_N$ avoids redundancies in the set of Slater determinants Θ_I. It follows that

$$\langle\Theta_I|\Theta_J\rangle=\delta_{IJ} . \tag{10}$$

In general, we adopt a multiconfiguration wave function Θ of the form

$$\Theta=\sum_I C_I\Theta_I ; \tag{11}$$

we assume that Θ is normalized to unity, namely

$$\langle\Theta|\Theta\rangle=1 . \tag{12}$$

The many-electron generalization of the Breit equation is

$$(\mathfrak{D}+\mathcal{B})\Theta=E\Theta , \tag{13}$$

where E is the total energy of the N-electron system. In view of Eq. (12), we have

$$E=\langle\Theta|\mathfrak{D}+\mathcal{B}|\Theta\rangle . \tag{14}$$

The Breit equation yields unsatisfactory results,[2] a difficulty often circumvented by determining Θ from the equation

$$\mathfrak{D}\Theta=E_D\Theta , \tag{15}$$

instead of from the generalized Breit equation. Other modifications to the Breit equation have been proposed by Brown and Ravenhall[12] and by Salpeter.[13] Here we shall proceed from the generalized Breit equation, pointing out the objectionable terms when we encounter them. Then the motivation for the proposal that Eq. (15) be used to determine Θ, instead of the generalized Breit equation, will be clear.

It is convenient to decompose the Dirac Hamiltonian in terms of powers of c, namely

$$\mathfrak{D}=c^2\mathfrak{M}+c\mathcal{P}+\mathcal{V} , \tag{16}$$

where [see Eqs. (1), (2)]

$$\mathfrak{M}=\sum_p \beta_p , \quad \mathcal{P}=\sum_p \vec{\alpha}_p\cdot\vec{p}_p ,$$
$$\mathcal{V}=\sum_p V_p+\tfrac{1}{2}\sum_p\sum_{q\neq p} 1/r_{pq} . \tag{17}$$

We introduce orbitals ω_i which satisfy the equation

$$\beta\omega_i=m_i\omega_i , \quad m_i=\pm 1 . \tag{18}$$

In case $m_i=1$, ω_i contains only a large component (the small component is zero), and in case $m_i=-1$, ω_i contains only a small component. Correspondingly, we introduce the Slater determinant Ω, where

$$\Omega=\{\omega_1\omega_2\ldots\omega_N\} . \tag{19}$$

Then we have

$$\mathfrak{M}\Omega=M\Omega , \tag{20}$$

where

$$M=\sum_i m_i=2k-N, \quad 0<k<N . \tag{21}$$

In Eq. (21), k is the number of orbitals with positive m_i, i.e., with large components only. We shall call M the *rest mass* of Ω. There are an infinite number of Ω's with the same rest mass, since Eq. (20) determines nothing of the space and spin behavior of Ω. In general, a wave function with rest mass M is a linear combination of Ω's with rest mass M.

We note that

$$[\mathfrak{M},\mathcal{V}]=0 \quad , \tag{22}$$

where the brackets indicate a commutator. Hence if Ω has rest mass M, so does $\mathcal{V}\Omega$. To deal with $\mathcal{P}$ and $\mathcal{B}$, we introduce the matrices $\vec{\alpha}^+$ and $\vec{\alpha}^-$, where

$$\vec{\alpha}^+=\begin{pmatrix}0 & \vec{\sigma}\\ 0 & 0\end{pmatrix} \quad , \quad \vec{\alpha}^-=\begin{pmatrix}0 & 0\\ \vec{\sigma} & 0\end{pmatrix} \quad . \tag{23}$$

We have the relations

$$\vec{\alpha}=\vec{\alpha}^+ + \vec{\alpha}^- \quad , \tag{24}$$

$$[\beta,\vec{\alpha}^\pm]=\pm 2\vec{\alpha}^\pm \quad . \tag{25}$$

In view of Eq. (24), we may write

$$\mathcal{P}=\mathcal{P}^+ + \mathcal{P}^- \quad , \tag{26}$$

$$\mathcal{B}=\mathcal{B}^+ + \mathcal{B}^0 + \mathcal{B}^- \quad , \tag{27}$$

where

$$\mathcal{P}^\pm=\sum_p \vec{\alpha}_p^\pm\cdot\vec{p}_p \quad , \tag{28}$$

$$\mathcal{B}^\pm=\tfrac{1}{2}\sum_p \sum_{q\neq p} b_{pq}^\pm \quad , \tag{29}$$

$$\mathcal{B}^0=\tfrac{1}{2}\sum_p \sum_{q\neq p} b_{pq}^0 \quad , \tag{30}$$

with

$$b_{pq}^\pm=-\tfrac{1}{2}[\,\vec{\alpha}_p^\pm\cdot\vec{\alpha}_q^\pm/r_{pq}+(\vec{\alpha}_p^\pm\cdot\vec{r}_{pq})(\vec{\alpha}_q^\pm\cdot\vec{r}_{pq})/r_{pq}^3] \quad , \tag{31}$$

$$b_{pq}^0=-\tfrac{1}{2}\{(\vec{\alpha}_p^+\cdot\vec{\alpha}_q^- + \vec{\alpha}_p^-\cdot\vec{\alpha}_q^+)/r_{pq} + [(\vec{\alpha}_p^+\cdot\vec{r}_{pq})(\vec{\alpha}_q^-\cdot\vec{r}_{pq})+(\vec{\alpha}_p^-\cdot\vec{r}_{pq})(\vec{\alpha}_p^+\cdot\vec{r}_{pq})]/r_{pq}^3\} \quad . \tag{32}$$

From Eq. (25) these relations follow:

$$[\mathfrak{M},\mathcal{P}^\pm]=\pm 2\mathcal{P}^\pm \quad , \tag{33}$$

$$[\mathfrak{M},\mathcal{B}^\pm]=\pm 4\mathcal{B}^\pm \quad , \tag{34}$$

$$[\mathfrak{M},\mathcal{B}^0]=0 \quad . \tag{35}$$

Hence, if Ω has rest mass M, so does $\mathcal{B}^0\Omega$, while $\mathcal{P}^\pm\Omega$ has rest mass $M\pm 2$, and $\mathcal{B}^\pm\Omega$ has rest mass $M\pm 4$.

These relations suggests a partition of Θ into $N+1$ component eigenfunctions of $\mathfrak{M}$, each with a different rest mass, while the decomposition of $\mathfrak{D}$, as given by Eq. (16), suggests a perturbation expansion in c^{-1} for these components. We expect the part of Θ of order c^0 to be an eigenfunction of $\mathfrak{M}$ with rest mass M. We anticipate that the parts of Θ of order c^{-1} will have rest masses $M\pm 2$, since $\mathcal{P}^+$ and $\mathcal{P}^-$ occur in $\mathfrak{D}$ multiplied by one power of c less than that multiplying $\mathfrak{M}$. Similarly, the parts of Θ of order c^{-2} will have rest masses M and $M\pm 4$, etc. Accordingly, we write

$$\Theta=\sum_{m=-(N+M)/2}^{(N-M)/2}\sum_{n=0}^{\infty} c^{-|m|-2n}\Theta_{mn} \quad , \tag{36}$$

where

$$\mathfrak{M}\Theta_{mn}=(M+2m)\Theta_{mn} \quad . \tag{37}$$

We also expand E in powers of c^{-2}:

$$E=c^2\sum_{n=0}^{\infty} c^{-2n}E_n \quad . \tag{38}$$

We substitute Eqs. (36) and (38) for Θ and E, respectively, in the generalized Breit equation, Eq. (13), and apply Eq. (37). $N+1$ equations result: one for each eigenvalue of $\mathfrak{M}$, each equation containing only functions of one particular rest mass. We equate powers of c^{-1} in these results. From the equation of order c^2, we find

$$(M-E_0)\Theta_{00}=0 \quad , \tag{39}$$

while the equations of order c give

$$(M-E_0\pm 2)\Theta_{\pm 1,0}+\mathcal{P}^\pm\Theta_{00}=0 \quad , \tag{40}$$

and the equations of order unity yield

$$(M-E_0\pm 4)\Theta_{\pm 2,0}+\mathcal{P}^\pm\Theta_{\pm 1,0}+\mathcal{P}^\pm\Theta_{00}=0 \quad , \tag{41}$$

$$(M-E_0)\Theta_{01}+\mathcal{P}^+\Theta_{-1,0}+\mathcal{P}^-\Theta_{10}+(\mathcal{V}+\mathcal{B}^0-E_1)\Theta_{00}=0 . \tag{42}$$

From these equations follow

$$M=E_0 \quad , \tag{43}$$

$$\Theta_{\pm 1,0}=\mp\tfrac{1}{2}\mathrm{P}^\pm\Theta_{00} \quad , \tag{44}$$

$$\Theta_{\pm 2,0}=\tfrac{1}{8}(\mathcal{P}^\pm)^2\Theta_{00}\mp\tfrac{1}{4}\mathcal{B}^\pm\Theta_{00} \quad , \tag{45}$$

$$(\mathcal{T}+\mathcal{V}+\mathcal{B}^0)\Theta_{00}=E_1\Theta_{00} \quad , \tag{46}$$

where

$$\mathcal{T}=\tfrac{1}{2}[\mathcal{P}^+,\mathcal{P}^-]=\tfrac{1}{2}\sum_p \beta_p\vec{p}_p^{\,2} \quad . \tag{47}$$

It is convenient to introduce Θ'_{01}, defined in terms of Θ_{00} and Θ_{01} by the equation

$$\Theta_{01}=-\tfrac{1}{8}(\mathcal{P}^+\mathcal{P}^-+\mathcal{P}^-\mathcal{P}^+)\Theta_{00}+\Theta'_{01} \quad . \tag{48}$$

We substitute Eq. (36) for Θ in the normalization condition, Eq. (12), and equate powers of c^{-1}. The equation of order c^0 is

$$\langle\Theta_{00}|\Theta_{00}\rangle=1 \quad , \tag{49}$$

while the equation of order c^{-2} becomes, after the substitution of Eqs. (44) and (48) for $\Theta_{\pm 1,0}$ and Θ_{01},

$$\langle\Theta'_{01}|\Theta_{00}\rangle+\langle\Theta_{00}|\Theta'_{01}\rangle=0 \quad . \tag{50}$$

The substitution of Eqs. (44), (45), and (48) for $\Theta_{\pm 1,0}$, $\Theta_{\pm 2,0}$, and Θ_{01} in Eq. (36) yields a compact approximate expression for Θ, namely

$$\Theta=[1+c^{-1}\mathcal{K}+\tfrac{1}{2}c^{-2}\mathcal{K}^2+\tfrac{1}{4}c^{-2}(\mathcal{B}^- - \mathcal{B}^+)]\Theta_{00}+c^{-2}\Theta'_{01}+O(c^{-3}) \quad , \tag{51}$$

where

$$\mathcal{K}=\tfrac{1}{2}(\mathcal{P}^- - \mathcal{P}^+)=\tfrac{1}{2}\textstyle\sum_p \vec{\alpha}_p\cdot\vec{p}_p\,\beta_p \quad . \tag{52}$$

We may evaluate E to order c^{-2} by simply using Eq. (51) to substitute for Θ in Eq. (14) and enforcing the normalization condition given by Eq. (12). We compare the resulting expression for E with that given by Eq. (38) to find

$$E_1 = \langle \Theta_{00} | \mathcal{T} + \mathcal{V} + \mathcal{B}^0 | \Theta_{00} \rangle \quad , \tag{53}$$

which is consistent with Eqs. (46) and (49). Proceeding with the evaluation of the second-order energy, we find, after dropping the objectionable term $\frac{1}{4}\langle \Theta_{00} | [\mathcal{B}^+, \mathcal{B}^-] | \Theta_{00} \rangle$,[14]

$$E_2 = \langle \mathcal{T}\Theta_{00} | \tfrac{1}{2}\mathcal{K}^2\Theta_{00} \rangle + \langle \tfrac{1}{2}\mathcal{K}^2\Theta_{00} | \mathcal{T}\Theta_{00} \rangle - \langle \tfrac{1}{2}\mathcal{K}^2\Theta_{00} | \mathcal{M} - E_0 | \tfrac{1}{2}\mathcal{K}^2\Theta_{00} \rangle + \langle \Theta_{00} | \mathcal{V} + \mathcal{B} | \tfrac{1}{2}\mathcal{K}^2\Theta_{00} \rangle + \langle \mathcal{K}\Theta_{00} | \mathcal{V} + \mathcal{B} | \mathcal{K}\Theta_{00} \rangle + \langle \tfrac{1}{2}\mathcal{K}^2\Theta_{00} | \mathcal{V} + \mathcal{B} | \Theta_{00} \rangle . \tag{54}$$

The objectionable term does not arise in the evaluation of E_2 if Eq. (45) is replaced by the equation

$$\Theta_{\pm 2,0} = \tfrac{1}{8} (\mathcal{P}^{\pm})^2 \Theta_{00} \quad , \tag{55}$$

omitting the term $\mp \frac{1}{4}\mathcal{B}^{\pm}\Theta_{00}$ occurring in Eq. (45). Clearly, Eq. (55) results instead of Eq. (45) if we start from Eq. (15) instead of the generalized Breit equation: This is the motivation for the proposal that Eq. (15) be used to determine Θ, instead of the generalized Breit equation. We conclude that Eq. (55) is correct and abandon Eq. (45).

Now Eq. (51) is replaced by the equation

$$\Theta = [1 + c^{-1}\mathcal{K} + \tfrac{1}{2}c^{-2}\mathcal{K}^2]\Theta_{00} + c^{-2}\Theta'_{01} + O(c^{-3}) \quad . \tag{56}$$

This equation gives the wave function to order c^{-2} in terms of Θ_{00} and Θ'_{01}; it is one of the central results of our treatment. Even without an evaluation of Θ'_{01}, it has application apart from the evaluation of the energy to order c^{-2}. For instance, if one supposes the large component of a relativistic orbital is given by φ_i, it follows from Eq. (56) that the small component is given, to order c^{-2}, by $\frac{1}{2}c^{-1}\vec{\sigma}\cdot\vec{p}\varphi_i$.

Since our treatment assumes relativistic effects are small, we may identify c^2E_0 as the rest-mass energy. Observable electrons always have positive rest mass, hence, the rest mass of an N-electron system should be N, i.e.,

$$E_0 = N \quad . \tag{57}$$

Combining this with Eq. (38), we give for the energy to order c^{-2}

$$E = c^2 N + E_1 + c^{-2}E_2 + \cdots \quad , \tag{58}$$

with E_1 given by Eq. (53) and E_2 given by Eq. (54).

Θ_{00} and Θ'_{01} consist only of Slater determinants which contain orbitals ω_i satisfying Eq. (18) and, in consequence of Eq. (57), only the possibility $m_i = 1$ may occur for these orbitals. Note that each term in $\mathcal{B}^0$ contains an operator $\vec{\alpha}_+$ which gives zero when operating on an orbital ω_i with $m_i = 1$. Hence $\mathcal{B}^0\Theta_{00}$ is zero, and the Breit operator does not contribute to the energy E_1. Since each orbital ω_i has positive m_i, only the large components are different from zero. A wave function Ψ can be derived from Θ_{00} by replacing each four-component ω_i in Θ_{00} by the corresponding large component φ_i, a two-component Pauli spinor. Then Eqs. (49), (46), and (53) go over into the equations

$$\langle \Psi | \Psi \rangle = 1 \quad , \tag{59}$$

$$\mathcal{H}\Psi = E_1\Psi \quad , \tag{60}$$

$$E_1 = \langle \Psi | \mathcal{H} | \Psi \rangle \quad , \tag{61}$$

respectively, where

$$\mathcal{H} = \sum_p [\tfrac{1}{2}\vec{p}_p^{\,2} + V_p] + \tfrac{1}{2}\sum_p \sum_{q\neq p} 1/r_{pq} \quad , \tag{62}$$

with the summations running from 1 to N. $\mathcal{H}$ is plainly the nonrelativistic Hamiltonian, hence Ψ and E_1 must be the nonrelativistic wave function and nonrelativistic energy, respectively.

Our expression for E_2 in terms of Θ_{00} likewise goes over into an expression in terms of Ψ. We find

$$E_2 = -\tfrac{1}{8}\textstyle\sum_p \langle \vec{p}_p^{\,2}\Psi | \vec{p}_p^{\,2}\Psi \rangle + \langle D_1\Psi | \Psi \rangle + \langle \Psi | D_1\Psi \rangle + \langle D_2\Psi | \Psi \rangle + \langle \Psi | D_2\Psi \rangle + \langle \Psi | F + G_0 + G_1 + G_2 | \Psi \rangle , \tag{63}$$

where

$$D_1 = -\tfrac{1}{8}\sum_p i\vec{\mathcal{E}}_p \cdot \vec{p}_p \quad , \tag{64}$$

$$D_2 = \tfrac{1}{8}\sum_p \sum_{q\neq p} i\vec{\mathcal{E}}_{pq} \cdot \vec{p}_p \quad , \tag{65}$$

$$F = \sum_p f_p \quad , \tag{66}$$

$$G_0 = \tfrac{1}{2}\sum_p \sum_{q\neq p} g_{0,pq} \quad , \tag{67}$$

$$G_1 = \tfrac{1}{2}\sum_p \sum_{q\neq p} g_{1,pq} \quad , \tag{68}$$

$$G_2 = \tfrac{1}{2}\sum_p \sum_{q\neq p} g_{2,pq} \quad , \tag{69}$$

with

$$\vec{\mathcal{E}}_p = i\vec{p}_p V_p \quad , \tag{70}$$

$$\vec{\mathcal{E}}_{pq} = i\vec{p}_p 1/r_{pq} \quad , \tag{71}$$

$$f_p = \tfrac{1}{2}(\vec{\mathcal{E}}_p \times \vec{p}_p)\cdot\vec{s}_p \quad , \tag{72}$$

$$g_{0,pq} = -\tfrac{1}{2}[r_{pq}^{-1}\vec{p}_p\cdot\vec{p}_q + r_{pq}^{-3}\vec{r}_{pq}\cdot(\vec{r}_{pq}\cdot\vec{p}_p)\vec{p}_q] \quad , \tag{73}$$

$$g_{1,pq} = \tfrac{1}{2}(\vec{\mathcal{E}}_{pq}\times\vec{p}_p)\cdot\vec{s}_p + \tfrac{1}{2}(\vec{\mathcal{E}}_{qp}\times\vec{p}_q)\cdot\vec{s}_q + (\vec{\mathcal{E}}_{pq}\times\vec{p}_p)\cdot\vec{s}_q + (\vec{\mathcal{E}}_{qp}\times\vec{p}_q)\cdot\vec{s}_p \quad , \tag{74}$$

$$g_{2,pq} = \vec{s}_p\cdot\vec{s}_q/r_{pq}^3 - 3(\vec{s}_p\cdot\vec{r}_{pq})(\vec{s}_q\cdot\vec{r}_{pq})/r_{pq}^5 \quad . \tag{75}$$

Here we have used $\vec{s}_p = \frac{1}{2}\vec{\sigma}_p$; notice that $\vec{\mathcal{E}}_p$ and $\vec{\mathcal{E}}_{pq}$ are the electric fields acting on the pth electron due to the nuclear charge and the qth electron, respectively.

Although we have integrated by parts to express E_2 in terms of the Hermitian operators f_p, $g_{0,pq}$, $g_{1,pq}$, and $g_{2,pq}$, we have not done so in the case of the integrals

$$\langle \vec{p}_p{}^2\Psi|\vec{p}_p{}^2\Psi\rangle \quad , \quad \langle D_1\Psi|\Psi\rangle + \langle\Psi|D_1\Psi\rangle \quad ,$$
$$\langle D_2\Psi|\Psi\rangle + \langle\Psi|D_2\Psi\rangle \quad .$$

The attempt to find a general expression for the integral $\langle \vec{p}_p{}^2\Psi|\vec{p}_p{}^2\Psi\rangle$ in terms of the expectation value of an operator is unprofitable.[4] This rules out the possibility of expressing E_2 as the expectation value of some operator. The integrals given in Eq. (63), however, are unambiguous and can be evaluated in a straightforward manner.

Integrals involving $-(\frac{8}{3}\pi)\vec{s}_p\cdot\vec{s}_q\delta^{(3)}(\vec{r}_{pq})$, which occur in other treatments, have here been eliminated in favor of simpler terms. As pointed out by de-Shalit and Talmi,[15] the integral involving $-(\frac{8}{3}\pi)\vec{s}_p\cdot\vec{s}_q\delta^{(3)}(\vec{r}_{pq})$ is equal to the integral involving $2\pi\delta^{(3)}(\vec{r}_{pq})$ whenever the wave function is antisymmetric with respect to the exchange of the pth and qth electrons. Accordingly we have the result

$$-\tfrac{1}{3}\sum_p\sum_{q\neq p}[\langle(i\vec{\mathcal{E}}_{pq}\cdot\vec{P}_p\Psi)|\vec{s}_p\cdot\vec{s}_q|\Psi\rangle + \langle\Psi|\vec{s}_p\cdot\vec{s}_q|(i\vec{\mathcal{E}}_{pq}\cdot\vec{P}_p\Psi\rangle] = 2[\langle D_2\Psi|\Psi\rangle + \langle\Psi|D_2\Psi\rangle] \quad . \tag{76}$$

This relation was used in deriving Eq. (63).

Classically, the quantity $-\frac{1}{8}\langle\vec{p}_p{}^2\Psi|\vec{p}_p{}^2\Psi\rangle$ gives the relativistic shift in mass of the pth electron due to its speed. f is the well-known spin-orbit coupling term due to the nuclear charge, coupling the electron with its own orbital moment with respect to the nucleus. The first two terms in g_1 are similar terms, with the nuclear charge replaced by that of another electron. The last two terms in g_1 couple the spin of one electron with the orbit of another electron. g_2 gives the spin-spin coupling. The quantities $\langle D_1\Psi|\Psi\rangle + \langle\Psi|D_1\Psi\rangle$ and $\langle D_2\Psi|\Psi\rangle + \langle\Psi|D_2\Psi\rangle$ have no obvious classical interpretation.

It is worth pointing out that although we have derived Ψ starting from the relativistic Θ, the starting point of calculations using the Pauli approximation will be Ψ. From this point of view, $\mathcal{H}$ rather than $\mathfrak{M}$ is the zeroth-order Hamiltonian, since the rest-mass energy is simply a constant. Then the relativistic effects constitute a simple perturbation on $\mathcal{H}$ (although this perturbation is not given by a Hamiltonian operator), yielding $c^{-2}E_2$ for the first-order perturbation correction to the energy.

III. ORBITAL INTEGRALS IN TERMS OF RADIAL INTEGRALS FOR ATOMS

We shall henceforth assume that the nonrelativistic wave function Ψ is constructed from two-component orbitals φ_i which are symmetry orbitals. In lieu of φ_i we introduce the notation $\varphi_{i\lambda\alpha a}$; the orbitals are defined by

$$\varphi_{i\lambda\alpha a}(r,\theta,\phi) = r^{-1}P_{\lambda i}(r)Y_{\lambda\alpha}(\theta,\phi)\eta_a \quad . \tag{77}$$

Here $Y_{\lambda\alpha}(\theta,\phi)$ is the conventional normalized spherical harmonic, and η_a is the two-component spin function with $m_s = a$. The index i now labels orbitals not distinguishable by symmetry. We also assume that the orbitals form an orthonormal set; hence we may write

$$\int_0^\infty dr\, P_{\lambda i}(r)P_{\lambda j}(r) = \delta_{ij} \quad . \tag{78}$$

Equation (77) allows us to integrate out the spin and angular dependence in the orbital integrals which arise in the evaluation of E_2, leaving integrals only over radial functions. The orbital integrals which arise in the evaluation of the nonrelativistic energy E_1 will not be treated here.

The radial integrals which emerge from the one-electron integrals are

$$\pi_{\lambda ij} = \tfrac{1}{8}\{-\int_0^\infty dr\,[P''_{\lambda i}(r) - \lambda(\lambda+1)r^{-2}P_{\lambda i}(r)] \times [P''_{\lambda j}(r) - \lambda(\lambda+1)r^{-2}P_{\lambda j}(r)] + Z[r^{-2}P_{\lambda i}(r)P_{\lambda j}(r)]_{r=0}\} \quad , \tag{79}$$

$$\zeta_{\lambda ij} = \tfrac{1}{2}Z\int_0^\infty dr\, r^{-3}P_{\lambda i}(r)P_{\lambda j}(r) \quad . \tag{80}$$

The prime indicates differentiation with respect to r. $\zeta_{\lambda ij}$ is similar to the usual notation for the single-electron spin-orbit coupling coefficient,[16] but it should be noted that the factor c^{-2} is not included. All of our expressions will be presented without this factor. We express the two-electron integrals in terms of the radial integrals given by

$$R_{\lambda i,\mu j;\rho k,\sigma l;\omega} = \int_0^\infty dr\int_0^r ds\,(rs)^{-1}U_\omega(r,s) \times P_{\lambda i}(r)P_{\mu j}(r)P_{\rho k}(s)P_{\sigma l}(s) \quad , \tag{81}$$

$$P_{\lambda i,\mu j;\rho k,\sigma l,\nu} = \int_0^\infty dr\int_0^\infty ds\,U_\nu(r,s) \times K_{\lambda i,\mu j;\nu}(r)P_{\rho k}(s)P_{\sigma l}(s) \quad , \tag{82}$$

$$Q_{\lambda i,\mu j;\rho k,\sigma l;\nu} = \tfrac{1}{2}\int_0^\infty dr\int_0^\infty ds\,W_\nu(r,s) \times K_{\lambda i,\mu j;\nu}(r)K_{\rho k,\sigma l;\nu}(s) \quad , \tag{83}$$

$$D_{\lambda i,\mu j,\rho k,\sigma l} = \tfrac{1}{4}\int_0^\infty dr\,r^{-2}P_{\lambda i}(r)P_{\mu j}(r)P_{\rho k}(r)P_{\sigma l}(r) \quad , \tag{84}$$

where

$$U_\nu(r,s) = \begin{cases} r^{-\nu-1}s^\nu, & s<r \\ s^{-\nu-1}r^\nu, & s>r \end{cases} \tag{85}$$

$$W_\nu(r,s) = rs[U_{\nu+1}(r,s)/(2\nu+3) - U_{\nu-1}(r,s)/(2\nu-1)] \quad , \tag{86}$$

$$K_{\lambda i,\mu j;\nu}(r)=k_{\lambda,\mu;\nu}P_{\lambda i}(r)\frac{\partial}{\partial r}[r^{-1}P_{\mu j}(r)]-k_{\mu,\lambda;\nu}P_{\mu j}(r)\frac{\partial}{\partial r}[r^{-1}P_{\lambda i}(r)]\ , \tag{87}$$

with

$$k_{\lambda,\mu;\nu}=\tfrac{1}{2}[\nu(\nu+1)+\lambda(\lambda+1)-\mu(\mu+1)]\times[\nu(\nu+1)]^{-1/2}; \tag{88}$$

it should be noted that $k_{\lambda,\lambda;0}=0$. Under interchange of shell indices, we have the following relations for these integrals:

$$\pi_{\lambda ij}=\pi_{\lambda ji}\ , \tag{89}$$

$$\zeta_{\lambda ij}=\zeta_{\lambda ji}\ , \tag{90}$$

$$R_{\lambda i,\mu j;\rho k,\sigma l;\omega}=R_{\mu j,\lambda i;\rho k,\sigma l;\omega}=R_{\lambda i,\mu j;\sigma l,\rho k;\omega}\ , \tag{91}$$

$$P_{\lambda i,\mu j;\rho k,\sigma l;\nu}=-P_{\mu j,\lambda i;\rho k,\sigma l;\nu}=P_{\lambda i,\mu j;\sigma l,\rho k;\nu}\ , \tag{92}$$

$$Q_{\lambda i,\mu j;\rho k,\sigma l;\nu}=-Q_{\mu j,\lambda i;\rho k,\sigma l;\nu}=-Q_{\lambda i,\mu j;\sigma l,\rho k;\nu}\ , \tag{93}$$

$$Q_{\lambda i,\mu j;\rho k,\sigma l;\nu}=Q_{\rho k,\sigma l;\lambda i,\mu j;\nu}\ , \tag{94}$$

$$D_{\lambda i,\mu j,\rho k,\sigma l}=D_{\mu j,\lambda i,\rho k,\sigma l}=D_{\rho k,\mu j,\lambda i,\sigma l}=D_{\sigma l,\mu j,\rho k,\lambda i}\ . \tag{95}$$

Note, however, that there is in general no relation between $R_{\lambda i,\mu j;\rho k,\sigma l;\omega}$ and $R_{\rho k,\sigma l;\lambda i,\mu j;\omega}$, nor between $P_{\lambda i,\mu j;\rho k,\sigma l;\nu}$ and $P_{\rho k,\sigma l;\lambda i,\mu j;\nu}$.

A. One-Electron Integrals

For atoms, we have

$$V_p=-Z/r_p\ , \tag{96}$$

hence, recalling Eq. (70),

$$\vec{\mathcal{E}}_p\cdot\vec{p}_p=-iZr_p^{-2}\frac{\partial}{\partial r_p}\ . \tag{97}$$

Then we easily find

$$\tfrac{1}{8}[-\langle\vec{p}_p^{\,2}\varphi_{i\lambda\alpha a}|\vec{p}_p^{\,2}\varphi_{j\mu\beta b}\rangle-\langle(i\vec{\mathcal{E}}_p\cdot\vec{p}_p\varphi_{i\lambda\alpha a})|\varphi_{j\mu\beta b}\rangle-\langle\varphi_{i\lambda\alpha a}|(i\vec{\mathcal{E}}_p\cdot\vec{p}_p\varphi_{j\mu\beta b})\rangle]=\delta_{\lambda\mu}\delta_{\alpha\beta}\delta_{ab}\pi_{\lambda ij}\ . \tag{98}$$

For the integral over f, we find

$$\langle\varphi_{i\lambda\alpha a}|f|\varphi_{j\mu\beta b}\rangle=\delta_{\lambda\mu}\langle\lambda\alpha|l_{\alpha-\beta}|\lambda\beta\rangle\langle b|s_{\alpha-\beta}|a\rangle\zeta_{\lambda ij}\ , \tag{99}$$

where the only nonvanishing components of l_γ and s_γ are given by

$$l_0=l_z\ ,\quad l_{\pm1}=\mp(2)^{-1/2}(l_x\pm il_y)\ ,$$
$$s_0=s_z\ ,\quad s_{\pm1}=\mp(2)^{-1/2}(s_x\pm is_y)\ . \tag{100}$$

Hence the angular part of Eq. (99) is just the expectation value of $\vec{1}\cdot\vec{s}$.

B. Two-Electron Integrals

For g_2 we have, from the results of Innes[17] (or the equivalent results of Horie[18]),

$$\langle\varphi_{i\lambda\alpha a}(1)\varphi_{k\rho\gamma c}(2)|g_{2,12}|\varphi_{j\mu\beta b}(1)\varphi_{l\sigma\delta d}(2)\rangle=C(1,1,2;b-a,d-c)\langle b|s_{b-a}|a\rangle\langle d|s_{d-c}|c\rangle$$
$$\times\sum_\omega(-1)^\omega[\tfrac{1}{5}\omega(\omega+1)(2\omega-1)(2\omega+1)(2\omega+3)]^{1/2}[C(\omega+1,\omega-1,2;\alpha-\beta,\beta+b+d-\alpha-a-c)\langle\lambda\alpha|C_{\omega+1,\alpha-\beta}|\mu\beta\rangle$$
$$\times\langle\rho\gamma|C_{\omega-1,\beta+b+d-\alpha-a-c}|\sigma\delta\rangle R_{\lambda i,\mu j;\rho k,\sigma l;\omega}+C(\omega-1,\omega+2,2;\alpha-\beta,\beta+b+d-\alpha-a-c)\langle\lambda\alpha|C_{\omega-1,\alpha-\beta}|\mu\beta\rangle$$
$$\times\langle\rho\gamma|C_{\omega+1,\beta+b+d-\alpha-a-c}|\sigma\delta\rangle R_{\rho k,\sigma l;\lambda i,\mu j;\omega}]\ , \tag{101}$$

where $C(\lambda\mu\nu;\alpha,\beta)$ is the Clebsch-Gordan coefficient in Rose's notation,[19] and $C_{\lambda\alpha}$ is the unnormalized spherical harmonic:

$$C_{\lambda\alpha}(\theta,\phi)=[4\pi/(2\lambda+1)]^{1/2}Y_{\lambda\alpha}(\theta,\phi)\ . \tag{102}$$

The summation over ω in Eq. (101) may be taken to run over all positive integers, but only terms in which the angular integrals do not vanish are different from zero. Hence, only values of ω for which both of the quantities $\lambda+\mu+\omega$ and $\rho+\sigma+\omega$ are *odd* integers contribute to the sum. It follows that the entire integral in Eq. (101) vanishes unless $\lambda+\mu+\rho+\sigma$ is an even integer; in other words, the matrix elements of g_2 are diagonal with respect to parity. The values of ω for which $R_{\lambda i,\mu j;\rho k,\sigma l;\omega}$ occurs in Eq. (101) are further restricted by the conditions

$$\lambda+\mu\geq\omega+1\geq|\lambda-\mu|\ ,$$
$$\rho+\sigma\geq\omega-1\geq|\rho-\sigma|\ . \tag{103}$$

The values of ω for which $R_{\rho k,\sigma l;\lambda i,\mu j;\omega}$ occurs are restricted by conditions similar to those given in Eq. (103), with λ and ρ interchanged and μ and σ interchanged. Note that the range of ω for which $R_{\rho k,\sigma l;\lambda i,\mu j;\omega}$ may occur can differ from the range of ω for which $R_{\lambda i,\mu j;\rho k,\sigma l;\omega}$ may occur.

We write

$$g_{1,12}=g'_{1,12}+g'_{1,21}\ , \tag{104}$$

where

$$g'_{1,12}=-\tfrac{1}{2}r_{12}^{-3}(\vec{r}_{12}\times\vec{p}_1)\cdot(\vec{s}_1+2\vec{s}_2)\ . \tag{105}$$

Then the results of Blume and Watson[20] yield

$$\langle\varphi_{i\lambda\alpha a}(1)\varphi_{k\rho\gamma c}(2)|g'_{1,12}|\varphi_{j\mu\beta b}(1)\varphi_{l\sigma\delta d}(2)\rangle=\tfrac{1}{2}(3)^{-1/2}(\delta_{cd}\langle b|s_{\alpha+\gamma-\beta-\delta}|a\rangle+2\delta_{ab}\langle d|s_{\alpha+\gamma-\beta-\delta}|c\rangle)$$
$$\times\textstyle\sum_\nu(-1)^\nu\langle\rho\gamma|C_{\nu,\gamma-\delta}|\sigma\delta\rangle\{(2\nu+1)^{1/2}C(\nu\nu1;\gamma-\delta,\alpha-\beta)\langle\lambda\alpha|C_{\nu,\alpha-\beta}|\mu\beta\rangle P_{\lambda i,\mu j;\rho k,\sigma l;\nu}$$
$$-\sum_{\omega=\nu\pm1}(2\nu+1)(2\omega+1)^{1/2}C(\nu\omega1;\gamma-\delta,\alpha-\beta)\langle\lambda\alpha|T^\nu_{\omega,\alpha-\beta}|\mu\beta\rangle$$
$$\times[\delta_{\omega,\nu+1}R_{\lambda i,\mu j;\rho k,\sigma l;\omega}-\delta_{\omega,\nu-1}R_{\rho k,\sigma l;\lambda i,\mu j;\omega}]\}\quad.\qquad(106)$$

Here we have introduced the operator $T^\nu\omega\alpha$, which operates on the angular coordinates θ and ϕ; it is given by the equation

$$T^\nu_{\omega\alpha}=\textstyle\sum_\beta C(\nu1\omega;\alpha-\beta,\beta)C_{\nu,\alpha-\beta}l_\beta\quad,\qquad(107)$$

hence[20]

$$\langle\lambda\alpha|T^\nu_{\omega\gamma}|\mu\beta\rangle$$
$$=\delta_{\alpha-\beta,\gamma}(-1)^{\nu-\omega}(2\mu+1)[(2\omega+1)\mu(\mu+1)/(2\lambda+1)]^{1/2}$$
$$\times\begin{Bmatrix}\nu&1&\omega\\ \mu&\lambda&\mu\end{Bmatrix}C(\mu\nu\lambda;00)C(\mu\omega\lambda;\beta,\alpha-\beta)\quad,\qquad(108)$$

where

$$\begin{Bmatrix}\nu&1&\omega\\ \mu&\lambda&\mu\end{Bmatrix}$$

is the $6-j$ symbol.[21] Nonzero terms in the summation over ν in Eq. (106) occur only when both $\lambda+\mu+\nu$ and $\rho+\sigma+\nu$ are *even* integers, hence the integral for g_1, like the integral for g_2, vanishes unless $\lambda+\mu+\rho+\sigma$ is an even integer. The range of nonzero terms in the summation over ν in Eq. (106) is further restricted by the conditions

$$\lambda+\mu\geq\nu\geq|\lambda-\mu|\quad,$$
$$\rho+\sigma\geq\nu\geq|\rho-\sigma|\quad.\qquad(109)$$

Note that the nonvanishing terms in $R_{\lambda i,\mu j;\rho k,\sigma l;\omega}$ occur only for values of ω satisfying Eq. (103) and that a similar situation holds for the terms in $R_{\rho k,\sigma l;\lambda i,\mu j;\omega}$.

In place of our integral $P_{\lambda i,\mu j;\rho k,\sigma l;\omega}$, Blume and Watson[20] use an expression which contains divergent integrals when $\nu=\lambda+\mu$ (unless $\lambda=\mu$). The integrals diverge because $P_{\lambda i}(r)$ and $P_{\mu j}(r)$ are proportional to $r^{\lambda+1}$ and $r^{\mu+1}$, respectively, in the neighborhood of $r=0$. A similar situation arises in the expressions given by Beck.[22] In the integral $P_{\lambda i,\mu j;\rho k,\sigma l;\nu}$ no divergences occur.

The general expression for the integral of g_0 is

$$\langle\varphi_{i\lambda\alpha a}(1)\varphi_{k\rho\gamma c}(2)|g_{0,12}|\varphi_{j\mu\beta b}(1)\varphi_{l\sigma\delta d}(2)\rangle=-\delta_{ab}\delta_{cd}\textstyle\sum_\nu[\langle\lambda\alpha|C_{\nu,\alpha-\beta}|\mu\beta\rangle\langle\sigma\delta|C_{\nu,\alpha-\beta}|\rho\gamma\rangle Q_{\lambda i,\mu j;\rho k,\sigma l;\nu}$$
$$+(2\nu+1)(\nu+2)^{-1}\langle\lambda\alpha|T^\nu_{\nu+1,\alpha-\beta}|\mu\beta\rangle\langle\sigma\delta|T^\nu_{\nu+1,\alpha-\beta}|\rho\gamma\rangle(R_{\lambda i,\mu j;\rho k,\sigma l;\omega}+R_{\rho k,\sigma l;\lambda i,\mu j;\omega})]\quad;\qquad(110)$$

the summation over ν proceeds as in Eq. (106). In case $\lambda i=\mu j=\rho k=\sigma l$, Eq. (110) gives Yanagawa's result.[23] Beck's results[22] imply Eq. (110) when the divergent integrals in his expressions are eliminated.

An integration by parts yield

$$\tfrac{1}{4}(\langle[i\vec{\mathcal{E}}_{12}\cdot\vec{\mathrm{p}}_1\varphi_{i\lambda\alpha a}(1)\varphi_{k\rho\gamma c}(2)]|\varphi_{j\mu\beta b}(1)\varphi_{l\sigma\delta d}(2)\rangle+\langle\varphi_{i\lambda\alpha a}(1)\varphi_{k\rho\gamma c}(2)|i\vec{\mathcal{E}}_{12}\cdot\vec{\mathrm{p}}_1\varphi_{j\mu\beta b}(1)\varphi_{l\sigma\delta d}(2)\rangle)$$
$$=\delta_{ab}\delta_{cd}D_{\lambda i,\mu j,\rho k,\sigma l}\textstyle\sum_\nu(2\nu+1)\langle\lambda\alpha|C_{\nu,\alpha-\beta}|\mu\beta\rangle\langle\sigma\delta|C_{\nu,\alpha-\beta}|\rho\gamma\rangle\quad,\qquad(111)$$

where the summation over ν proceeds as in Eq. (106).

IV. REDUCED-MATRIX ELEMENTS

Since the radial function $P_{\lambda i}(r)$ introduced in Eq. (77) is the same for all values of α and a, there are $4\lambda+2$ orbitals $\varphi_{i\lambda\alpha a}$ characterized by the same radial function $P_{\lambda i}(r)$. This set is an *electron shell*, labeled by the combination index λi.

From the available orbitals, one can construct N-electron Slater determinants (SD's); each SD is completely characterized by the particular orbitals used for its construction, which are called the *occupied orbitals* in that SD. The number of occupied orbitals of a shell in a particular SD is called the *occupation number* of the shell in that SD. Obviously, the occupation number of the shell λi in any SD is $\leq 4\lambda+2$; when the equality applies, the shell λi is called a *closed shell* of the SD, otherwise an open shell. An *electron configuration* is the collection of all SD's which have the same shell occupation numbers. Hence, a set of occupation numbers defines a configuration completely, although in general it only partially characterizes the SD's of a configuration.

An electron configuration can be resolved into N-electron functions which belong to definite symmetry species and subspecies. These N-electron functions are linear combinations of the SD's of a configuration; we call them *configuration state functions* (CSF's).[24] We introduce for the CSF's the notation Φ_{ASLJMP}. Each CSF is an eigenfunction of $\vec{S}^2, \vec{L}^2, \vec{J}^2$, J_z, and $\mathcal{I}$ (parity). The operators $\vec{J}^2$, J_z, and $\mathcal{I}$ commute with the *relativistic* Hamiltonian $\mathcal{D}$ (and with the Breit operator $\mathcal{B}$), hence J, M, and P are "good" quantum numbers. The operators $\vec{S}^2$ and $\vec{L}^2$ only commute with the *nonrelativistic* Hamiltonian, hence S and L are, strictly speaking, not good quantum numbers. The index A labels CSF's not distinguishable by their values of S, L, J, M, and P. CSF's with the same values of S, L, J, M, and P, but from different configurations, have different values of A; so do different CSF's arising from the same configuration with the same values of S, L, J, M, and P, when this is possible.

In many cases, a CSF arising from a particular configuration is uniquely specified by its values of S, L, J, and M (the value of P can always be deduced from the set of configuration occupation numbers). Important examples are configurations which have at most one open s and/or one open p shell. On the other hand, for multiple open p shells and for open d or f shells this is no longer always the case. A simple example is the configuration $2p^2 3p$. All of the CSF's from this configuration have $P=-1$. The CSF's arising from this configuration are uniquely determined by the specification of S, L, J, and M for the cases where S and L indicate ^2S, ^4S, ^4P, ^4D, or ^2F. On the other hand, there are three independent ^2P CSF's, with the $2p$ orbitals coupled to form a ^1S, ^1D, or ^3P function; similarly there are two independent ^2D CSF's, with the $2p$ orbitals coupled to form a ^3P or ^1D function. In these cases the index A for the CSF Φ_{ASLJMP} not only indicates the configuration $2p^2 3p$, but also serves to distinguish between the three possible ^2P CSF's, or between the two possible ^2D CSF's.

The use of CSF's that are eigenfunctions of $\vec{L}^2$ and $\vec{S}^2$ allows an application of the Wigner-Eckart theorem:[25] The dependence on J of the matrix elements with respect to the SCF's may be factored out in terms of a single $6-j$ symbol,[26] allowing us to write, for instance,

$$\langle ASLMP|F|A'S'L'J'M'P'\rangle = \delta_{JJ'}\delta_{MM'}\delta_{PP'}(-1)^{L+S'+J}\begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}\langle ASLP|F|A'S'L'P\rangle \quad . \tag{112}$$

The quantity $\langle ASLP|F|A'S'L'P\rangle$ is the *reduced-matrix element* of F. As our notation suggests, it is independent of the values of J and M, although it still depends on other details of the construction of the two CSF's, including the values of S and L and of S' and L'. In similar fashion, we write

$$-\tfrac{1}{8}\sum_p \langle \vec{p}_p^{\,2}\Phi_{ASLJMP}|\vec{p}_p^{\,2}\Phi_{A'S'L'J'M'P'}\rangle + \langle D_1\Phi_{ASLJMP}|\Phi_{A'S'L'J'M'P'}\rangle + \langle\Phi_{ASLJMP}|D_1\Phi_{A'S'L'J'M'P'}\rangle$$
$$= \delta_{JJ'}\delta_{MM'}\delta_{PP'}\delta_{SS'}\delta_{LL'}\langle ASLP|\Pi_1|A'SLP\rangle \quad , \tag{113}$$

$$\langle D_2\Phi_{ASLJMP}|\Phi_{A'S'L'J'M'P'}\rangle + \langle\Phi_{ASLJMP}|D_2\Phi_{A'S'L'J'M'P'}\rangle = \delta_{JJ'}\delta_{MM'}\delta_{PP'}\delta_{SS'}\delta_{LL'}\langle ASLP|\Pi_2|A'SLP\rangle \quad , \tag{114}$$

$$\langle ASLJMP|G_0|A'S'L'J'M'P'\rangle = \delta_{JJ'}\delta_{MM'}\delta_{PP'}\delta_{SS'}\delta_{LL'}\langle AS\,LP|G_0|A'SLP\rangle \quad , \tag{115}$$

$$\langle ASLJMP|G_1|A'S'L'J'M'P'\rangle = \delta_{JJ'}\delta_{MM'}\delta_{PP'}(-1)^{L+S'+J}\begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}\langle ASLP|G_1|A'S'L'P\rangle \quad , \tag{116}$$

$$\langle ASLJMP|G_2|A'S'L'J'M'P'\rangle = \delta_{JJ'}\delta_{MM'}\delta_{PP'}(-1)^{L+S'+J}\begin{Bmatrix} L & S & J \\ S' & L' & 2 \end{Bmatrix}\langle ASLP|G_2|A'S'L'P\rangle \quad . \tag{117}$$

These relations constitute a considerable simplification, allowing the matrix elements to be computed for all values of J with little more effort than that required for a single value of J.

The matrix elements given in Eqs. (113)–(115) vanish unless $L=L'$ and $S=S'$. However, nonzero matrix elements of F, G_1, and G_2 for which $L'\neq L$ and/or $S'\neq S$ do exist, hence an accurate wave function describing an atomic state is not in general an eigenfunction of $\vec{L}^2$ and $\vec{S}^2$. For a large number of cases, however, wave functions with definite L and S provide excellent approximations (Russell-Saunders coupling), and the matrix elements with $L\neq L'$ and/or $S'\neq S$ may be neglected. Then the relativistic corrections simply remove the degeneracy with respect to J of the nonrelativistic energy. This case is our primary concern in this paper.

In this case the wave function Ψ is an eigenfunction of $\vec{L}^2$ and $\vec{S}^2$; we append the quantum numbers,

S, L, J, M and P, writing Ψ_{SLJMP}. Our expansion of the wave function in terms of the CSF's may be written

$$\Psi_{SLJMP} = \sum_A \Phi_{A\,SLJMP} C_{ASLP} \quad . \tag{118}$$

We can always choose the CSF's such that the expansion coefficients become real; we assume this to be done. Note that the expansion coefficients C_{ASLP} do not depend on the quantum numbers J and M.

We combine our expression of Ψ_{SLJMP} in terms of the CSF's with our previous results to find

$$E_{2,SLJP} = \overline{E}_{2,SLP} + (-1)^{L+S+J} \begin{Bmatrix} L & S & J \\ S & L & 1 \end{Bmatrix} (\langle \Psi_{SLP} | F | \Psi_{SLP} \rangle + \langle \Psi_{SLP} | G_1 | \Psi_{SLP} \rangle) + (-1)^{L+S+J} \begin{Bmatrix} L & S & J \\ S & L & 2 \end{Bmatrix} \langle \Psi_{SLP} | G_2 | \Psi_{SLP} \rangle \quad , \tag{119}$$

where

$$\overline{E}_{2,SLP} = \sum_{AA'} C_{ASLP} (\langle ASLP | \Pi_1 | A'SLP \rangle + \langle ASLP | \Pi_2 | A'SLP \rangle + \langle ASLP | G_0 | A'SLP \rangle) C_{A'SLP} \quad , \tag{120}$$

$$\langle \Psi_{SLP} | F | \Psi_{SLP} \rangle = \sum_{AA'} C_{ASLP} \langle ASLP | F | A'SLP \rangle \, C_{A'SLP} \quad , \tag{121}$$

$$\langle \Psi_{SLP} | G_1 | \Psi_{SLP} \rangle = \sum_{AA'} C_{ASLP} \langle ASLP | G_1 | A'SLP \rangle \, C_{A'SLP} \quad , \tag{122}$$

$$\langle \Psi_{SLP} | G_2 | \Psi_{SLP} \rangle = \sum_{AA'} C_{ASLP} \langle ASLP | G_2 | A'SLP \rangle \, C_{A'SLP} \quad . \tag{123}$$

The entire dependence of $E_{2,SLJP}$ on J is contained in the 6-j symbols in Eq. (119). Hence, from the properties of the 6-j symbols, we find the relation

$$\overline{E}_{2,SLP} = [(2S+1)(2L+1)]^{-1} \sum_J (2J+1) E_{2,SLJP} \quad , \tag{124}$$

so $\overline{E}_{2,SLP}$ is the average first-order relativistic correction to the energy of the J multiplet, as was suggested by our notation.

In the case of Russell-Saunders coupling, where Eq. (119) holds, $E_{2,SLJP}$ would follow the Landé interval rule with respect to J if the term proportional to $\langle \Psi_{SLP} | G_2 | \Psi_{SLP} \rangle$ were absent, since for $L \neq 0$ and $S \neq 0$,

$$(-1)^{L+S+J} \begin{Bmatrix} L & S & J \\ S & L & 1 \end{Bmatrix} = \frac{1}{2} \frac{J(J+1) - L(L+1) - S(S+1)}{[L(L+1)(2L+1)S(S+1)(2S+1)]^{1/2}} \quad .$$

As pointed out by Araki,[27] the terms proportional to $\langle \Psi_{SLP} | G_2 | \Psi_{SLP} \rangle$ cause a deviation from the Landé interval rule even in the case of Russell-Saunders coupling, as may be seen from the relation

$$(-1)^{L+S+J} \begin{Bmatrix} L & S & J \\ S & L & 2 \end{Bmatrix} = \frac{3[J(J+1) - L(L+1) - S(S+1)][J(J+1) - L(L+1) - S(S+1) + 1] - 4S(S+1)L(L+1)}{2[L(L+1)(2L-1)(2L+1)(2L+3)S(S+1)(2S-1)(2S+1)(2S+3)]^{1/2}}$$

for $S=1$ and $L=1$.

V. MATRIX ELEMENTS OF THE FIRST-ORDER RELATIVISTIC CORRECTIONS TO THE ENERGY IN TERMS OF RADIAL INTEGRALS

The matrix elements and reduced-matrix elements with respect to the CSF's arising from the first-order relativistic correction to the energy can be expressed in terms of the corresponding one- and two-electron orbital integrals. We have dealt with these orbital integrals in Sec. III. In accord with our results there we write

$$\langle ASLP | \Pi_1 | A'SLP \rangle = \sum_{\lambda i j} s_{ASLP, A'SLP; \lambda i j} \pi_{\lambda i j} \quad , \tag{125}$$

$$\langle ASLP | F | AS'L'P \rangle = \sum_{\lambda i j} t_{ASLP, A'S'L'P; \lambda i j} \zeta_{\lambda i j} \quad , \tag{126}$$

$$\langle ASLP | \Pi_2 | A'SLP \rangle = \sum_{\lambda i} \sum_{\mu j} \sum_{\rho k} \sum_{\sigma l} d_{ASLP, A'SLP; \lambda i, \mu j, \rho k, \sigma l} D_{\lambda i, \mu j, \rho k, \sigma l} \quad , \tag{127}$$

$$\langle ASLP|G_0|A'SLP\rangle = \sum_{\lambda i}\sum_{\mu j}\sum_{\rho k}\sum_{\sigma l}\Big(\sum_{\omega} r_{0;ASLP,A'SLP;\lambda i,\mu j;\rho k,\sigma l;\omega}R_{\lambda i,\mu j;\rho k,\sigma l;\omega} + \sum_{\nu} q_{ASLP,A'SLP;\lambda i,\mu j;\rho k,\sigma l;\nu}Q_{\lambda i,\mu j;\rho k,\sigma l,\nu}\Big) \quad , \qquad (128)$$

$$\langle ASLP|G_1|A'S'L'P\rangle = \sum_{\lambda i}\sum_{\mu j}\sum_{\rho k}\sum_{\sigma l}\Big(\sum_{\omega} r_{1;ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\omega}R_{\lambda i,\mu j;\rho k,\sigma l;\omega} + \sum_{\nu} p_{ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\nu}P_{\lambda i,\mu j;\rho k,\sigma l;\nu}\Big) \quad , \qquad (129)$$

$$\langle ASLP|G_2|A'S'L'P\rangle = \sum_{\lambda i}\sum_{\mu j}\sum_{\rho k}\sum_{\sigma l}\sum_{\omega} r_{2;ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\omega}R_{\lambda i,\mu j;\rho k,\sigma l;\omega} \quad . \qquad (130)$$

The radial integrals appearing here are defined in Eqs. (79)–(84); the summations over ω and ν proceed as in Eqs. (101) and (106), respectively.

The coefficients $s_{ASLP,A'SLP;\lambda ij}$, $t_{ASLP,A'S'L'P;\lambda ij}$, $d_{ASLP,A'SLP;\lambda i,\mu j,\rho k,\sigma k}$, $r_{0;ASLP;A'SLP;\lambda i,\mu j;\rho k,\sigma l;\omega}$, $r_{1;ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\omega}$, $r_{2;ASLP;A'SLP;\lambda i,\mu j;\rho k,\sigma l;\omega}$, $q_{ASLP;A'SLP;\lambda i,\mu j;\rho k,\sigma l;\nu}$, and $p_{ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\nu}$ characterize the angular and spin parts of the various relativistic corrections to the energy. They depend only on the details of the construction of the CSF's from Slater determinants. For simple cases, their derivation, with the help of the results given in Sec. III, is usually not a difficult matter; however, general formulas for them, particularly the coefficients originating from the two-electron integrals, can be only obtained by an elaborate analysis involving Clebsch-Gordan and/or Racah algebra, and this will not be attempted here. Note that the nonvanishing coefficients for any particular case are actually rather sparse. For example, in the case $ASLP = A'S'L'P$, $s_{ASLP,ASLP;\lambda ij}$, and $t_{ASLP,ASLP;\lambda ij}$ vanish unless $i=j$, while $d_{ASLP,ASLP;\lambda i,\mu j,\rho k,\sigma l}$, $r_{n;ASLP,ASLP;\lambda i,\mu j;\rho k,\sigma l;\omega}$ $(n=0,\ 1,\ 2)$, $q_{ASLP,ASLP;\lambda i,\mu j;\rho k,\sigma l;\nu}$, and $p_{ASLP,ASLP;\lambda i,\mu j;\rho k,\sigma l;\nu}$ all have nonzero values only in case $\lambda i=\mu j$, $\rho k=\sigma l$, or in the cases $\lambda i=\rho k$, $\mu j=\sigma l$, and $\lambda i=\sigma l$, $\mu j=\rho k$. Note also that $S_{ASLP,ASLP;\lambda ii}$ is simply the occupation number of the shell λi in the CSF indexed by ASLP.

We note also the relation

$$r_{0;ASLP,A'SLP;\lambda i,\mu j;\rho k,\sigma l;\omega} = r_{0;ASLP,A'SLP;\rho k,\sigma l;\lambda i,\mu j;\omega} \quad , \qquad (131)$$

which follows from Eq. (109). However, no similar relation exists in general for $r_{1,ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\omega}$ or for $r_{2;ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\sigma l;\omega}$.

In practical calculations, CSF's with closed shells are a frequent occurrence.[28] Simplifications then apply which we give here. We suppose that there is some shell ρk for which

$$s_{ASLP,ASLP;\rho kk} = s_{A'S'L'P,A'S'L'P;\rho kk} = 4\rho + 2 \quad ; \qquad (132)$$

that is, that some shell ρk is a closed shell in both the CSF labeled by $ASLP$ and the CSF labeled by $A'S'L'P$ (the case $ASLP = A'S'L'P$ is not excluded). Then we have[28]

$$t_{ASLP,A'S'L'P;\rho kk} = 0 \quad , \qquad (133)$$

and, in accord with Elliott's results,[29]

$$r_{2;ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\rho k;\omega} = 0 \quad ,$$
$$r_{2;ASLP,A'S'L'P;\rho k,\rho k;\lambda i,\mu j;\omega} = 0 \quad , \qquad (134)$$
$$r_{2;ASLP,A'S'L'P;\lambda i,\rho k;\mu j;\rho k;\omega} = 0 \quad ,$$

for all values of λi, μj, and ω. From the results of Blume and Watson[20] and Beck,[22] we have

$$p_{ASLP,A'S'L'P;\lambda i,\mu j;\rho k,\rho k;\nu} = 0 \quad ,$$
$$r_{1;ASLP;A'S'L'P;\lambda i,\mu j;\rho k,\rho k;\omega} = -\tfrac{1}{2}\delta_{\lambda\mu}\delta_{\omega,1}t_{ASLP,A'S'L'P;\lambda ij}(4\rho+2) \quad , \qquad (135)$$

$$r_{1,ASLP,A'S'L'P;\rho k,\rho k;\lambda i,\mu j;\omega} = 0 \quad ;$$

$$p_{ASLP,A'S'L'P;\lambda i,\rho k;\mu j,\rho k;\nu} = \tfrac{1}{4}\delta_{\lambda\mu}t_{ASLP,A'S'L'P;\lambda ij} \times (4\rho+2)3[\lambda(\lambda+1)]^{-1}k_{\lambda,\rho;\nu}x_{\lambda\rho\nu} \quad , \qquad (136)$$

$$r_{1,ASLP,A'SLP;\lambda i,\rho k;\omega} = \tfrac{1}{4}\delta_{\lambda\mu}t_{ASLP,A'S'L'P;\lambda ij}(4\rho+2)3[\lambda(\lambda+1)]^{-1}v_{\lambda\rho\omega} \quad .$$

Here $k_{\lambda,\mu;\nu}$ is given by Eq. (88) and $x_{\lambda\mu\nu}$ is given by

$$x_{\lambda\mu\nu} = \tfrac{1}{2}B_{\lambda+\mu-\nu}B_{\lambda+\nu-\mu}B_{\mu+\nu-\lambda}/[(\lambda+\mu+\nu+1)B_{\lambda+\mu+\nu}] \,, \qquad (137)$$
$$B_{2\sigma} = (2\sigma)!/(\sigma!)^2 \quad ,$$

when $\lambda+\mu+\nu$ is an even integer; $x_{\lambda\mu\nu}$ vanishes if $\lambda+\mu+\nu$ is odd. Also, we have used

$$v_{\lambda\mu\omega} = \tfrac{1}{4}[\omega(\omega+1)]^{-1}(\lambda+\mu+\omega+1)(\lambda+\mu-\omega+1) \times (\lambda+\omega-\mu)(\mu+\omega-\lambda)x_{\lambda\mu\omega-1} \quad . \qquad (138)$$

For the orbit-orbit coupling coefficients, we find

$$r_{0;ASLP,A'SLP;\lambda i,\mu j;\rho k,\rho k;\omega} = 0 \quad ,$$
$$r_{0;ASLP,A'SLP;\lambda i,\rho k;\mu j,\rho k;\omega} = -\tfrac{1}{4}\delta_{\lambda\mu}s_{ASLP,A'SLP;\lambda ij}(4\rho+2)v_{\lambda\rho\omega} \quad ,$$

TABLE I. Fine-structure splittings in cm^{-1}.

	Blume and Watson[a]	Malli[b]	This work, Hartree-Fock	Experiment
$B(^2P_{3/2}-^2P_{1/2})$	14.6		15.16	16
$C(^3P_1-^3P_0)$	15.8	16.17	16.18	16.4
$C(^3P_2-^3P_1)$	25.8	26.59	26.56	27.1
$N(^2D_{5/2}-^2D_{3/2})$	−13.6		−12.97	−8
$N(^2P_{3/2}-^2P_{1/2})$	−5.5		−5.09	0
$O(^3P_1-^3P_0)$	−72.7	−73.69	−73.62	−68.0
$O(^3P_2-^3P_1)$	−162	−163.94	−163.83	−158.5
$F(^2P_{3/2}-^2P_{1/2})$	−397		−402.2	−404.0
$Al(^2P_{3/2}-^2P_{1/2})$	90.8		92.72	112.04
$Si(^3P_1-^3P_0)$	64.5	66.17	65.10	77.15
$Si(^3P_2-^3P_1)$	128	129.03	128.95	146.16
$S(^3P_1-^3P_0)$	−183	−181.89	−181.61	−176.8
$S(^3P_2-^3P_1)$	−369	−366.95	−366.35	−396.8
$Cl(^2P_{3/2}-^2P_{1/2})$	−818		−822.9	−881

[a]See Ref. 32. [b]See Ref. 33.

$$q_{ASLP,A'SLP,\lambda i,\rho k;\mu j,\rho k;\nu} = -\tfrac{1}{4}\delta_{\lambda\mu}s_{ASLP,A'SLP;\lambda ij}(4\rho+2)x_{\lambda\rho\nu} \quad , \quad (139)$$

except in case $\lambda i=\mu j=\rho k$; in that case we find

$$r_{0;ASLP;A'SLP;\rho k,\rho k;\rho k,\rho k;\omega} = -\tfrac{1}{2}s_{ASLP,A'SLP;\rho kk}(4\rho+2)v_{\rho\rho\omega} \quad . \quad (140)$$

Equations (139) and (140) are consistent with the results of Beck.[22] Note that the occurrence of the factor $\frac{1}{4}$ in Eqs. (136) and (138) compensates for the fourfold occurrence of such terms in the summations given in Eqs. (128) and (129). Finally, we have

$$d_{ASLP,A'SLP;\lambda i,\mu j,\rho k,\rho k} = \tfrac{1}{2}\left[\tfrac{1}{6}\delta_{\lambda\mu}s_{ASLP,A'SLP;\lambda ij}(4\rho+2)\right], \quad (141)$$

unless $\lambda i=\mu j=\rho k$, where we have

$$d_{ASLP,A'SLP;\rho k,\rho k,\rho k,\rho k} = \tfrac{1}{4}s_{ASLP,A'SLP;\rho kk}(4\rho+2) \quad . \quad (142)$$

The factor $\frac{1}{6}$ in Eq. (141) compensates for the sixfold occurrence of such terms in Eq. (127).

VI. NUMERICAL APPLICATION

A. Hartree-Fock Results

We have computed the first-order relativistic corrections to the energy for the ground states of the atoms He through Ar, and for the two lowest excited states each of C, N, and O. The analytic Hartree-Fock wave functions of Cohen[30] were used for He through Ne and Malli's wave functions[31] were used for Na through Ar. In Table I we present our results for the fine-structure splittings and compare them with the previous results of Blume and Watson[32] and Malli,[33] and with experimental values.[34] In Table II we present the parts of the relativistic corrections to the energy which do not contribute to the fine-structure splitting. These are the quantities $c^{-2}\overline{E}_2$, where $\overline{E}_2$ is defined in Eq. (120).

Essentially the same formalism was used for all of the computed results in Table I, but different wave functions were used in each case. The analytic wave functions we have used are characterized by carefully chosen basis functions and should prove quite accurate. The close agreement between our results and Malli's results, based on numerical wave functions, confirms this. [Note that Malli's results omit B, $N(^2D)$, $N(^2P)$, F, Al, and Cl.] The earlier results of Blume and Watson are based on analytic wave functions of poorer accuracy.

Our results in Tables I and II were all computed with wave functions which exactly satisfy the cusp condition.[35] Additional computations were made using wave functions[36] in which the cusp condition was relaxed, but were otherwise of comparable accuracy. These resulted in virtually the same values for the fine-structure splittings as those we have given. There is, however, a difference in the computed value of $c^{-2}\overline{E}_2$ of about 2% or 3% for atoms in the first row of the periodic table; for example, for $N(^4S)$ we obtain $c^{-2}\overline{E}_2=-0.026926$, while the value from the exact cusp wave function is -0.026545. This difference comes mainly from the different values obtained for the integrals $\pi_{\lambda ij}$

TABLE II. Average relativistic corrections to the energy in a.u.

	Nonrelativistic energy[a]	Average relativistic correction $c^{-2}\overline{E}_2$
$He(^1S)$	−2.861 680	−0.000 064 842
$Li(^2S)$	−7.432 726	−0.000 052 552
$Be(^1S)$	−14.573 02	−0.002 114 8
$B(^2P)$	−24.529 06	−0.005 893 3
$C(^3P)$	−37.688 61	−0.013 343
$C(^1D)$	−37.631 32	−0.013 359
$C(^1S)$	−37.549 60	−0.013 369
$N(^4S)$	−54.400 92	−0.026 545
$N(^2D)$	−54.296 15	−0.026 440
$N(^2P)$	−54.228 07	−0.026 432
$O(^3P)$	−74.809 38	−0.047 540
$O(^1D)$	−74.729 26	−0.047 576
$O(^1S)$	−74.611 01	−0.047 534
$F(^2P)$	−99.409 34	−0.079 573
$Ne(^1S)$	−128.547 0	−0.125 67
$Na(^2S)$	−161.858 84	−0.191 87
$Mg(^1S)$	−199.614 61	−0.283 12
$Al(^2P)$	−241.876 64	−0.403 40
$Si(^3P)$	−288.854 29	−0.560 00
$P(^4S)$	−340.718 71	−0.759 52
$S(^3P)$	−397.504 72	−1.009 57
$Cl(^2P)$	−459.481 97	−1.318 04
$Ar(^1S)$	−526.817 44	−1.694 00

[a]From Refs. 30 and 31.

TABLE III. Total Hartree-Fock energies in a.u.

	Relativistic Hartree-Fock[a]	This work $E_1+c^{-2}E_2$
He	−2.8617	−2.861745
Be	−14.5752	−14.57513
Ne	−128.6753	−128.6727
Ar	−528.5513	−528.51144

[a]See Ref. 38.

[defined in Eq. (79)] for the orbitals of s symmetry, which seems to be caused by different behavior of these orbitals near $r=0$ in the two cases. It is the exact cusp wave function that gives the more accurate description near $r=0$, and hence the more accurate value of $c^{-2}\overline{E}_2$.

When relativistic effects are small, there should be good agreement between our Hartree-Fock results and results from relativistic Hartree-Fock calculations of the type outlined by Kim.[37] In Table III we compare our results for the sum $E_1+c^{-2}E_2$ with the total energy, including the Breit correction terms, obtained by Mann and Johnson,[38] for the atoms He, Be, Ne, and Ar. It should be noted that their relativistic Hartree-Fock results include energy corrections of order c^{-4}, c^{-6}, etc. which come from the Dirac Hamiltonian and the Breit operator, while our results omit such terms. Since their calculations omit other higher-order energy corrections (e.g., the Lamb-shift correction), it is not at all clear that their results actually improve on ours.

B. Multiconfiguration Results for Nitrogen

For most of the atoms in the first row of the periodic table, the Hartree-Fock results given in Table I are in good agreement with experiment. The most noticeable discrepancies occur for the nitrogen ^2D and ^2P states. Hence these states provide a good testing ground for multiconfiguration results for the fine-structure splittings.

The wave functions used here were computed using a multiconfiguration self-consistent-field (MC-SCF) formalism of the type put forward by Hinze and Roothaan,[24] in which the orbitals and CSF expansion coefficients are simultaneously optimized. The radial functions $P_{\lambda i}(r)$ are expansions in terms of normalized Slater-type basis functions, namely

$$P_{\lambda i}(r)=\sum_p R_{\lambda p}(r)c_{\lambda i p} \quad ,$$
$$R_{\lambda p}(r)=[2\zeta_{\lambda p})^{2n}\lambda p^{+1}/(2n_{\lambda p})]^{1/2}r^{n\lambda p}e^{-\zeta_{\lambda p}r} \quad . \tag{143}$$

The basis functions were taken from the results of Bagus and Gilbert[36] for the nitrogen ^2D and ^2P states; the ζ's were not reoptimized. The radial functions for our wave functions are given in Table IV, together with the nonrelativistic energies and the values for $c^{-2}\overline{E}_2$.

The CSF expansion coefficients are given in Table V. The nitrogen ^2D wave function consists of CSF's from the configurations $1s^22s^22p^3$, $1s^22s^22p^23p$, and $1s^22s^23p^22p$. The nitrogen ^2P wave function contains CSF's from these configurations and also from the configurations $1s^22p^5$ and $1s^22s^23s^22p$. Note that only ^2P CSF's arise from the last two configurations. Since we have required that the ^2D wave function be orthogonal to the ^2D function

$$1s^22s^2(1/\sqrt{2})[2p^2(^3P)3p-2p^2(^1D)3p]$$

the five CSF expansion coefficients provide only four independent variational parameters. The substitution $2p\to 2p+\epsilon 3p$ yields

$$2p^3\,{}^2D\to 2p^3\,{}^2D+\sqrt{3}\epsilon(1/\sqrt{2})\{[2p^2(^3P)3p\,{}^2D] - [2p^2(^1D)3p\,{}^2D]\}+O(\epsilon^2) \quad ,$$

hence our constraint on the ^2D wave function corresponds to the exclusion of the function coming

TABLE IV. Energies and radial functions for MC-SCF N(^2D) and N(^2P).

Nitrogen ^2D: $E_0=-54.31429$, $c^{-2}\overline{E}_2=-0.026914$									
n	ζ	c_{1s}	c_{2s}		n	ζ	c_{2p}	c_{3p}
1	10.595	0.110750	0.001260		2	7.693	0.008103	0.025191
1	6.026	0.929642	−0.266426		2	3.272	0.225920	−0.682047
3	7.332	−0.042260	−0.030465		2	1.877	0.438952	−0.774379
2	2.528	0.002159	0.539124		2	1.168	0.414068	1.430358
2	1.586	−0.000088	0.554662					
Nitrogen ^2P: $E_0=-54.28665$, $c^{-2}\overline{E}_2=-0.026943$								
n	ζ	c_{1s}	c_{2s}	c_{3s}	n	ζ	c_{2p}	c_{3p}
1	10.592	0.111253	0.002583	0.010633	2	7.748	0.007716	0.024814
1	6.022	0.932954	−0.255389	−0.338239	2	3.275	0.226397	−0.613019
3	7.323	−0.042279	−0.032453	−0.239912	2	1.865	0.451033	−0.825028
2	2.527	−0.005195	0.550576	2.512475	2	1.131	0.405991	1.432865
2	1.589	−0.007302	0.544268	−2.251829				

TABLE V. CSF expansion coefficients for MC-SCF $N(^2D)$ and $N(^2P)$.

$N(^2D)$		$N(^2P)$	
$1s^2\,2s^2\,2p^3$	0.995 871	$1s^2\,2s^2\,2p^3$	0.978 718
$1s^2\,2s^2\,2p^2(^3P)3p$	0.014 176	$1s^2\,2s^2\,2p^2(^1S)\,3p$	−0.028 881
$1s^2\,2s^2\,2p^2(^1D)\,3p$	0.014 176	$1s^2\,2s^2\,2p^2(^3P)\,3p$	−0.024 768
$1s^2\,2s^2\,3p^2(^3P)2p$	−0.051 748	$1s^2\,2s^2\,2p^2(^1D)\,3p$	0.006 861
$1s^2\,2s^2\,3p^2(^1D)2p$	0.071 852	$1s^2\,2s^2\,3p^2(^1S)\,2p$	−0.064 996
		$1s^2\,2s^2\,3p^2(^3P)\,2p$	0.051 006
		$1s^2\,2s^2\,3p^2(^1D)\,2p$	0.054 263
		$1s^2\,2p^5$	0.174 074
		$1s^2\,2s^2\,3s^2\,2p$	0.023 747

from the "single replacement" of a $2p$ function by a $3p$ function in $2p^3\,{}^2D$. For the same reason, we have required the ^2P wave function to be orthogonal to the ^2P function

$$\tfrac{1}{3}(1/\sqrt{2})1s^2 2s^2\{2[2p^2(^1S)3p]-3[2p^2(^3P)3p]-\sqrt{5}[2p^2(^1D)3p]\}\;;$$

hence the nine CSF expansion coefficients provide only eight independent variational parameters.

Our wave functions for the nitrogen ^2D and ^2P are much too crude to be considered accurate descriptions of the electronic states to which they pertain. Accordingly, our results must be regarded as only preliminary, to be confirmed by calculations with more accurate wave functions. Still, the fine-structure splittings for the nitrogen ^2D and ^2P states computed with these wave functions are a substantial improvement over the Hartree-Fock results, as may be seen from Table VI. This is perhaps not unreasonable, in view of the quite good agreement with experiment already obtained with a Hartree-Fock wave function in the case of the carbon fine-structure splitting.

The situation can perhaps be made more plausible by observing that in carbon the addition of the CSF

TABLE VI. Nitrogen fine-structure splittings in cm^{-1}.

	Hartree-Fock	MC-SCF	Experiment
$^2D_{5/2}-{}^2D_{3/2}$	−12.97	−9.23	−8
$^2P_{3/2}-{}^2P_{1/2}$	−5.09	−0.34	0

from the configuration $(1s)^2(2s)^2 2p3p$ does not improve the wave function, since a version of Brillouin's theorem[39] applies. This argument breaks down in nitrogen, since there is more than one ^2D or ^2P CSF which can come from the configuration $(1s)^2(2s)^2(2p)^2 3p$. The addition of such a CSF can influence the one-electron nuclear spin-orbit contribution and the contributions from the two-electron integrals containing $1s$-shell and $2s$-shell functions (which behave in many respects as corrections to the one-electron integral ζ_{Mf}). Ordinarily, these contributions to the fine-structure splitting are the major part, although the remainder is not negligible; for example, in the carbon Hartree-Fock calculation for the $^3P_2$-$^3P_1$ splitting these two parts amount to 32.36 and −5.80 cm^{-1}, respectively. Thus, the addition of such a CSF can have a much greater influence on the calculation of the fine-structure splitting than would be the case for most CSF's. In fact, our calculations indicate that the major part of the difference between the Hartree-Fock results and the MC-SCF results presented here may be attributed to the addition of CSF's from the configuration $1s^2 2s^2 2p^2 3p$.

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Second-Order Corrections to the Fine Structure of Helium*

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The fine-structure constant can be determined to high accuracy from precise measurements of the fine structure of the $2\,^3P$ level in helium. One of the necessary calculations is to compute the contributions from the six Breit operators and the mass-polarization operator in second-order perturbation theory. The eighteen spin-dependent perturbations from intermediate ^3P states are calculated by solving an inhomogeneous Schrödinger equation for the perturbation of the wave function by the variational method. The second-order contributions are then given by a single integral. These corrections are calculated using standard Hylleraas expansions with up to 165 terms for the perturbed wave functions, resulting in contributions to the two fine-structure intervals of the order of 10^{-4} cm^{-1}, but only four of the results are sufficiently accurate.

I. INTRODUCTION

Today there are several accurate values of the Sommerfeld fine-structure constant $\alpha = e^2/\hbar c \simeq \frac{1}{137}$ obtained from high-precision measurements of the atomic energy levels of hydrogen and deuterium. These levels can be calculated to any desired accuracy (in principle, at least) from quantum electrodynamics (QED) as a power series in α (and $\log\alpha$), and thus α can be determined experimentaly. The classic results are those of Lamb and co-workers,[1] who measured the $2P_{1/2}$-$2P_{3/2}$ fine-structure separation in deuterium. Using their value and a theoretical formula by Layzer,[2] Cohen and Du Mond[3] obtained $\alpha^{-1} = 137.0388(6)$ for their tabulation of the fundamental constants. The most widely used value of α today is probably the one given by Parker, Taylor, and Langenberg[4] in their tabulation of the fundamental constants. They obtained $\alpha^{-1} = 137.036\,02(21)$, i.e., an accuracy of 1.5 ppm, from measuring $2e/h$ by the ac Josephson effect.[5]

Helium is better suited to high-accuracy experiments than hydrogenic atoms, because the $2\,^3P$