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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 experimentally. 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 $2\,^3P$

state (of He[4]) has a lifetime of about 10^{-7} sec and a fine-structure comparable to the $2\,^2P$ state of deuterium which only has a lifetime of about 7×10^{-9} sec. The natural linewidth for the $2\,^3P$ state of helium is thus about 3 MHz, whereas for the $2\,^2P$ state of deuterium (or hydrogen) it is about 100 MHz. So one can measure the fine-structure intervals of the $2\,^3P$ state of helium with an accuracy higher than anything possible for hydrogenic fine structures. There are furthermore, two fine-structure intervals in the fine structure of the $2\,^3P$ level, and α can in principle be determined from either one. The smaller interval has been measured to[6,7] $\nu_{12}=2291.196(5)$ MHz or 2.2 ppm and the larger interval to $\nu_{01}=29616.864(36)$ MHz or 1.2 ppm.[8]

Since the fine-structure intervals are proportional to the square of α (to lowest order in α) one can in principle obtain α to less than 1 ppm from these helium data. For comparison we quote the result of Kaufman $et\ al.$,[9] $\alpha^{-1}=137.0350(4)$, obtained from hydrogen fine structure, and thus only good to 3 ppm.

However, there is at present no theoretical formula for the fine structure of helium with terms up to and including the order $\alpha^6 mc^2$, such as there is, say, for hydrogen.[2] To bring the theory of the helium atom up to the same level of accuracy as current experiments, theorists face a formidable task. As outlined by Schwartz,[10,11] this project consist of several fairly distinct jobs.

Formally, the energy levels are given by a power series in α^2:

$$E_J - E_0 = \alpha^2 \langle 0 \mid H_2 \mid 0 \rangle_J$$

$$+ \alpha^4 \langle 0 \mid H_2 [1/(E_0 - H_0)] H_2 \mid 0 \rangle_J + \alpha^4 \langle 0 \mid H_4 \mid 0 \rangle_J$$

$$+ \text{(terms of order } \alpha^5 \text{ and higher).} \quad (1)$$

Here H_0, E_0, and $\mid 0 \rangle$ are the nonrelativistic Hamiltonian, the energy of the (unperturbed) $2\,^3P$ state in atomic energy units, $2\Re = mc^2\alpha^2$, and the corresponding nonrelativistic wave function, respectively:

$$H_0 \mid 0 \rangle = E_0 \mid 0 \rangle .$$

The subscript J denotes spin dependence where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum ($J = 0, 1$, and 2). H_2 are the lowest-order corrections to the nonrelativistic Hamiltonian, the so-called Breit operators,[12-14] which are well known. There are both spin-dependent (spin-spin and spin-orbit) and spin-independent Breit operators. In first-order perturbation theory only the former contribute to the fine-structure separations, but in second-order perturbation theory both contribute, since the spin-independent operators mix with the spin-dependent ones to give a spin-dependent result. Finally, H_4 are higher-order corrections to

the Hamiltonian.

There are then four main jobs to be done. First, since the left-hand side of (1) is known experimentally to 1 or 2 ppm, we want to know the leading term on the right-hand side of (1) to 1 ppm. This task has been accomplished by Schwartz,[10] who evaluated the expectation values of the spin-dependent Breit operators for a sequence of variational wave functions $\mid 0 \rangle$, with up to 439 terms in the expansion. Second, we want to determine the calculation of the second-order perturbation energies

$$\langle 0 \mid H_2^{(1)} [1/(E_0 - H_0)] H_2^{(2)} \mid 0 \rangle , \quad (2)$$

where $H_2^{(1)}$ ($H_2^{(2)}$), say, is spin-dependent, but $H_2^{(2)}$ ($H_2^{(1)}$) can be any Breit operator. Since α^2 is of the order 10^{-4} we only need this term, as well as the expectation value of H_4, to an accuracy of 1%; and terms of α^5 and higher order in (1) can be ignored. This is the task which we shall begin in this paper. Third, we want the determination of the operator H_4. This is probably the most difficult of the four projects (the other three are mainly computational problems), requiring much QED know-how. However, a simplifying feature is that only spin-dependent operators are required. A first attempt at this analysis was made by Kim,[14] and a more complete analysis, starting from the Bethe-Salpeter equation, has just been completed by Douglas.[15] Finally, the fourth job is to evaluate the expectation value of H_4 to 1%. This work has recently been done by Daley.[16]

In addition to the terms in (1) there are other corrections owing to the anomalous magnetic moment of the electron [which gives a α^3 term in (1)] which are quite simple; then the reduced mass must be inserted, and also the operator[17] $\vec{p}_1 \cdot \vec{p}_2 / M$ that corrects for the motion of the nucleus, which contributes in second-order perturbation theory when mixed with the spin-dependent Breit operators. We will treat it along with the spin-independent Breit operators. Finally, there are a number of more subtle nuclear (strong-interaction) corrections; one may hope to take over most of the results[18] from hydrogen. Schwartz[10] has given arguments to show that a finite charge distribution of the nucleus, smeared over nuclear distances, as well as vacuum-polarization modifications to the nuclear potential, have negligible effects.

Since there are some discrepancies between theory and experiment in QED, the large amount of theoretical and numerical work required for the completion of this project seems eminently worthwhile.

II. METHOD

The second-order energy (2) is usually evaluated

by inserting a complete set of states:

$$\sum_n{}' \frac{\langle 0 \mid H_2^{(1)} \mid n\rangle\langle n \mid H_2^{(2)} \mid 0\rangle}{E_0 - E_n} ,$$

but this is not practical for the present problem since we do not have a complete set of helium wave functions. Instead we solve an inhomogeneous Schrödinger equation for the perturbation to the wave function. This is formulated as a variational principle, so that one gets a problem similar to the original Hylleraas problem of finding the ground-state nonrelativistic helium wave function, except that in the present case there is no unknown energy eigenvalue. Once the perturbation to the wave function has been found, the second-order perturbation energy (2) is given by a single integral.

The Schrödinger equation is

$$(H_0 + \lambda H_1)\Psi = E\Psi , \tag{3}$$

where H_0 is the nonrelativistic Hamiltonian for helium. In atomic units where the unit of length is $a_0 = \hbar^2/me^2$ and the unit of energy is $e^2/a_0 = \alpha^2 mc^2 = 2\Re$ we have

$$H_0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12} , \tag{4}$$

where $Z = 2$. H_1 are the Breit operators. Expanding the energy E and the wave function Ψ in powers of the "parameter of smallness" λ (in this case $\lambda = \alpha^2$), inserting the expansion in (4), and equating coefficients of powers of λ one obtains an inhomogeneous differential equation for the perturbation to the wave function. Since H_1 is a sum of operators, $H_1 = \sum_i H_1^{(i)}$, there are mixed ($i \neq j$) and unmixed ($i = j$) second-order energies

$$E_2^{(i,j)} = \frac{\langle\Psi_0 \mid H_1^{(i)} - E_1^{(i)} \mid \Psi_1^{(j)}\rangle}{\langle\Psi_0 \mid \Psi_0\rangle} , \tag{5}$$

where the equation for $\Psi_1^{(j)}$ is

$$(H_0 - E_0)\Psi_1^{(j)} = -(H_1^{(j)} - E_1^{(j)})\Psi_0 \tag{6}$$

and

$$E_1^{(i)} = \frac{\langle\Psi_0 \mid H_1^{(i)} \mid \Psi_0\rangle}{\langle\Psi_0 \mid \Psi_0\rangle} . \tag{7}$$

Equations (5), (6), and (7) are the fundamental equations for obtaining the second-order energies $E_2^{(i,j)}$ when E_0 and Ψ_0 are known. The homogeneous equation corresponding to (6) has Ψ_0 as a solution, so the addition of a multiple of Ψ_0 to $\Psi_1^{(j)}$ is seen to leave $E_2^{(i,j)}$ unchanged because of (7).

Equation (6) is solved approximately by the variational method. Consider the functional

$$E_2[\Psi_1^{(i)}, \Psi_1^{(j)}]$$
$$= \langle\Psi_1^{(i)} \mid H_0 - E_0 \mid \Psi_1^{(j)}\rangle + \langle\Psi_1^{(i)} \mid H_1^{(j)} - E_1^{(j)} \mid \Psi_0\rangle$$
$$+ \langle\Psi_0 \mid H_1^{(i)} - E_1^{(i)} \mid \Psi_1^{(j)}\rangle . \tag{8}$$

The variational principle

$$\frac{\delta}{\delta\Psi_1^{(i)}} E_2[\Psi_1^{(i)}, \Psi_1^{(j)}] = 0$$

with respect to $\Psi_1^{(i)}$ gives Eq. (13) for $\Psi_1^{(j)}$ and the value of the functional (8) is then just the second-order energy $E_2^{(i,j)}$ [Eq. (11)], apart from normalization. Variation with respect to $\Psi_1^{(j)}$ gives the adjoint of Eq. (6) for $\Psi_1^{(i)}$; the value of the functional E_2 is then $E_2^{(j,i)}$. Once the solutions $\Psi_1^{(i)}$ and $\Psi_1^{(j)}$ have been obtained we have four different ways of calculating (numerically) the same physical quantity $E_2^{(i,j)} = E_2^{(j,i)}$ for $i \neq j$ (for $i = j$ we have two ways):

$$E_2^{(i,j)}\langle\Psi_0 \mid \Psi_0\rangle$$
$$= -\langle\Psi_1^{(i)} \mid H_0 - E_0 \mid \Psi_1^{(j)}\rangle = -\langle\Psi_1^{(j)} \mid H_0 - E_0 \mid \Psi_1^{(i)}\rangle$$
$$= \langle\Psi_0 \mid H_1^{(i)} - E_1^{(i)} \mid \Psi_1^{(j)}\rangle = \langle\Psi_1^{(i)} \mid H_1^{(j)} - E_1^{(j)} \mid \Psi_0\rangle . \tag{9}$$

Comparison of the numerical result obtained the four different ways will indicate the seriousness of round-off errors.

The method of solution is the usual one of setting up a sequence of functions to approximate $\Psi_1^{(i)}$, each sequence consisting of a sum of terms U_n with coefficients $x_n^{(i)}$ as linear parameters:

$$\Psi_1^{(i)} \approx \psi^{(i)} = \sum_{n=1}^{N} x_n^{(i)} U_n ,$$

which turns (6) into a system of N inhomogeneous linear equations for $x_1^{(i)}, \ldots, x_N^{(i)}$:

$$\sum_{k=1}^{N} [\langle U_l \mid H_0 \mid U_k\rangle - E_0\langle U_l \mid U_k\rangle]x_k^{(i)} = b_l^{(i)} ,$$
$$l = 1, 2, \ldots, N \tag{10}$$

where

$$b_l^{(i)} = -\langle U_l \mid H_1^{(i)} \mid \Psi_0\rangle + E_1^{(i)}\langle U_l \mid \Psi_0\rangle . \tag{11}$$

We do not use functions U_n that form an orthonormal set. The accuracy of the computed second-order energies will be judged by how well (or badly) they converge as the number N of trial functions increases.

The choice of these trial functions will be guided by the ones used for the variational solution Ψ_0 of the homogeneous nonrelativistic Schrödinger equation. We will calculate the second-order energies using the trial functions employed for the variational solution of the ordinary Schrödinger equation; these functions are called the standard bases. Because of the singular nature of the Breit operators as $r_1 \to 0$, $r_2 \to 0$, or $r_{12} \to 0$, the left-hand side of (13) will be less singular than the right-hand side, i.e., $H_0 U_n$ ($n = 1, 2, \ldots, N$) will not reproduce the singularities of $H_1^{(i)}\Psi_0$, and this will in general manifest itself by slow convergence of $E_2^{(i,j)}$ as N increases. Therefore, one shall have eventually to introduce trial functions which have singularities as $r_1 \to 0$,

$r_2 \to 0$, or $r_{12} \to 0$, in addition to the terms in the standard basis. Once Ψ_0 is known, one can determine what extra functions V_m are needed from the requirement that $H_0 V_m$ shall have the same leading singularities at $r_1 \to 0$, $r_2 \to 0$, and $r_{12} \to 0$ as $H_1^{(i)} \Psi_0$.

This approach to second-order perturbation theory,[19] sometimes called the method of Dalgarno and Lewis,[20] has been used to calculate the second-order Stark effect in hydrogen and the perturbation on a hydrogen atom of a far-away charge. It was investigated by Schwartz[21] in a series of papers, culminating with a very accurate calculation of the nonrelativistic Lamb shift in hydrogen (Bethe sum), and has also been used by Schwartz[22] to calculate the Bethe sum in helium. In these hydrogen problems, exact solutions for Ψ_1 in closed form were obtained; in the case of the helium Lamb shift, a variational solution for Ψ_1 (for each value of the photon momentum) was used.

III. NONRELATIVISTIC WAVE FUNCTION

To start the calculations we need the nonrelativistic wave function Ψ_0 which is the solution of

$$H_0 \Psi_0 = E_0 \Psi_0 , \tag{12}$$

with H_0 given by (4). The time-honored variational method is used. The functions chosen for the standard triplet-P basis are (Hylleraas basis)

$$U_{lmn} = \frac{1 - P_{12}}{4\pi \sqrt{2}} \vec{r}_1 r_1^m r_2^n r_{12}^l e^{-1/2\kappa\sigma r_1} e^{-1/2\kappa r_2} , \tag{13}$$

where $l \geq 0$, $m \geq 0$, $n \geq 0$. The variational wave functions are

$$\Psi_0 \approx \psi_0 = \sum_{l,m,n=0}^{l+m+n \geq \omega} C_{lmn} U_{lmn} , \tag{14}$$

where the coefficients C_{lmn} are determined from the variational principle. In (13), P_{12} exchanges coordinates r_1 and r_2, and the P-state character is given by the vector sign.

This type of triplet-P wave functions were used by Schwartz[10] to calculate the expectation values of the spin-dependent Breit operators; with $\omega = 10$ and 286 terms in expansion (14) the results were accurate to 1 part in 10^4. While this fell short of the goal of 1 ppm, these functions should be quite adequate for the present purpose since we only need an accuracy of 1% in the final answers. With an expanded basis, obtained from (14) by the replacement $C_{lmn} \to C_{lmn} + D_{lmn} (r_1 + r_2)^{1/2}$, the goal of calculating the leading term of the fine structure to 1 ppm was achieved with a 439-term wave function, but the computations had to be done in 52-decimal arithmetic. Wave functions (14) have been used by the author[23] to calculate the three reduced-matrix elements determining the hyperfine structure of the $2\,^3P$ level in helium 3 (which has nuclear spin $\frac{1}{2}$);

with 165 terms the accuracy was about 0.5%.

The three basic variables are thus the two nucleon-electron distances r_1 and r_2 and the interelectron distance

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2| = (r_1^2 + r_1^2 - 2r_1 r_2 \cos\theta_{12})^{1/2} ,$$

where θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_2$. Wave functions are computed for $\omega = 1, 2, \ldots, 8$. The number of terms in the expansion (13), i.e., the number of different choices of (l, m, n) such that $0 \leq l + m + n \leq \omega$ when $l \geq 0$, $m \geq 0$, and $n \geq \omega$ is

$$N(\omega) = \tfrac{1}{6}(\omega + 1)(\omega + 2)(\omega + 3) . \tag{15}$$

The variational-principle equivalent to the Schrödinger equation (12) is

$$\delta \langle \Psi_0 | H_0 - E_0 | \Psi_0 \rangle = 0 . \tag{16}$$

Approximating the lowest triplet-P wave function Ψ_0 by an expansion ψ_0 of the form (14), the variational principle (16) gives

$$\delta \left[\sum_{k=1}^{N(\omega)} \sum_{j=1}^{N(\omega)} C_k C_j (\langle U_k | H_0 | U_l \rangle - E_0 \langle U_k | U_l \rangle) \right] = 0 , \tag{17}$$

where $(l, m, n) \to k$; the so-called "natural" order is used. This means that the $\tfrac{1}{2}(\omega + 1)(\omega + 2)$ possible values of (l, m, n) such that $l + m + n = \omega$, with $l \geq 0$, $m \geq$ and $n \geq 0$ are mapped one-to-one into a range of k values given by $N(\omega - 1) < k \leq N(\omega)$. Variation with respect to the coefficients C_k gives a symmetric eigenvalue problem; using an obvious notation, we have

$$\sum_{k=1}^{N} [(H_0)_{lk} - E_0 I_{lk}] C_k = 0, \quad l = 1, 2, \ldots, N(\omega). \tag{18}$$

We seek the lowest eigenvalue $E_0 = E_0(\omega)$ and corresponding eigenvector $(C_1, C_2, \ldots, C_{N(\omega)})$ in this problem. The approximate wave function $\psi_0 \approx \Psi_0$ is then given by (14). The eigenvalue problem was solved by an approximate iterative method, described by Schwartz.[10]

Ideally, the screening parameters $\kappa\sigma$ and κ should also be varied. However, differentiating the expression in square brackets in (17) with respect to $\kappa\sigma$ and κ gives a huge expression, and the resulting two equations would be highly nonlinear and impossible to solve for $\kappa\sigma$ and κ. To obtain the best values of κ and σ, i.e., those which give the lowest eigenvalue E_0, one must proceed by trial and error. For each guess of $(\kappa\sigma, \kappa)$ the matrices $(H_0)_{kl}$ and I_{kl} must be calculated, which requires the computation of many integrals; then the secular Eq. (18) must be solved. This should be done for each value of ω, since there is no reason for the optimum values of $\kappa\sigma$ and κ, for one value of ω, to be optimum at another value of ω. We did not perform this variation, but used Schwartz's[10] values of κ and σ for all values of ω[24]:

$\kappa = 4.62, \quad \sigma = 0.29$.

These two numbers are the only input for the calculations reported here. Schiff $et\,al.$[25] calculate wave functions and expectation values of the Breit operators for several states in helium, varying their screening parameters. However, using a 560-term wave function (with only integer powers of their variables) and varying the screening parameters, they did not match the accuracy of Schwartz's calculation of the fine-structure intervals that he obtained using 439 terms, with half-powers, but keeping the screening parameters constant. We therefore conclude that for an accuracy of 1%, the values of κ and σ may be kept constant.

IV. MODEL PROBLEM

The procedure for obtaining second-order perturbation energies can be tested on a simple case where the answers are known. The nonrelativistic Hamiltonian is $H_0 = T + V$, where T is the kinetic energy and V the potential energy. If we take T and V as perturbations,

$$H_1^{(1)} = V \quad \text{and} \quad H_1^{(2)} = T,$$

then it is known that

$$E_1^{(1)} = 2E_0, \quad E_1^{(2)} = -E_0, \quad E_2^{(1,1)} = E_2^{(2,2)} = E_0,$$

$$E_2^{(1,2)} = E_2^{(2,1)} = -E_0 . \tag{19}$$

These relations can be deducted from a simple scaling argument. In cgs units the Hamiltonian is

$$(H_0)_{\text{cgs}} = (\hbar^2/m)(T)_{\text{a.u.}} + e^2(V)_{\text{a.u.}} , \tag{20}$$

where $(T)_{\text{a.u.}}$ and $(V)_{\text{a.u.}}$ are T and V in atomic units. The Hamiltonian $H = H_0 + \lambda T + \mu V = (1 + \lambda)\,T + (1 + \mu)V$, where λ and μ are "parameters of smallness," has the spectrum of H_0 in scaled units; since the energy unit is $e^2/a_0 = me^4/\hbar^2$, it follows from (20) that the scaling factor is $(1 + \mu)^2/(1 + \lambda)$. Thus the perturbed Hamiltonian H has a perturbed energy level

$$E = E_0 \,\frac{(1 + \mu)^2}{1 + \lambda} \approx E_0(1 + 2\mu - \lambda + \mu^2 + \lambda^2 - 2\mu\lambda). \tag{21}$$

Relations (19) follow from (21).

Because H_0 is just the sum of the two perturbations, $H_0 U_n$ will reproduce the singularities of $H_1^{(i)}\Psi_0 \approx H_1^{(i)}\Psi_0$ $(i = 1, 2)$, so the standard basis (13) should be adequate for the expansion of $\Psi_1^{(i)}$. There are no singularities in this calculation to slow down the convergence of $E_2^{(i,j)}$ as ω increases.

The calculation of matrix elements $(H_0)_{kl}$ of H_0 (and thus also of T and V) between a pair of elements in the standard basis is described in Appendix B. The inhomogeneous system of equations (16) to be solved is

$$\sum_{k=1}^{N(\omega)} A_{lk}X_k^{(i)} = b_l^{(i)} , \quad l = 1, 2, \ldots, N(\omega) \tag{22}$$

where $A_{lk} = (H_0)_{lk} - E_0(\omega')I_{lk}$. Here $E_0(\omega')$ is the approximation to E_0 obtained when $N(\omega')$ terms are used in the expansion (14) for Ψ_0; using this variational wave function in (11), the right-hand side of (22) becomes

$$b_l^{(i)} = -\sum_{n=1}^{N(\omega)} C_n[(H_1^{(i)})_{ln} - E_1^{(i)}I_{ln}] , \tag{23}$$

where

$$E_1^{(i)} = \left[\sum_{m=1}^{N(\omega')} \sum_{n=1}^{N(\omega')} C_n C_m (H_1^{(i)})_{nm} \right] \Big/ \langle \Psi_0 \mid \Psi_0 \rangle \tag{24}$$

and

$$\langle \Psi_0 \mid \Psi_0 \rangle = \sum_{m=1}^{N(\omega')} \sum_{n=1}^{N(\omega')} C_n C_m I_{nm} . \tag{25}$$

The second-order energies $E_2^{(i,j)}$ in (9) are given by

$$E_2^{(i,j)} \langle \Psi_0 \mid \Psi_0 \rangle$$

$$= -\sum_{m=1}^{N(\omega')} X_m^{(i)} \left(\sum_{n=1}^{N(\omega')} X_n^{(j)} [(H_0)_{nm} - E_0(\omega')I_{nm}] \right)$$

$$= -\sum_{n=1}^{N(\omega)} b_n^{(i)} X_n^{(j)} ; \tag{26}$$

there are similar expressions for $E_2^{(j,i)}$.

If $\omega = \omega'$, then $E_0(\omega')$ has a value which makes the matrix A_{lk} singular [see Eq. (18)]. We could try to avoid this complication by keeping ω' bigger (smaller) than the largest (smallest) value of ω for which $\Psi_1^{(i)}$ and $E_2^{(i,j)}$ are calculated. But in any case $E_0(\omega)$ is quite close to $E_0(\omega')$, and one would have to solve an "almost singular" system of linear equations, and this can be very unpleasant numerically. It is also preferable to have $\omega' = \omega$ in the calculations for each value of ω, so that the second-order energies are obtained by exactly the same algorithm for each value of ω. So the same number of standard terms are used in the expansions for $\Psi_1^{(i)}$ and Ψ_0. The singular matrix A_{kl} then has rank $N(\omega) - 1$, because $E_0(\omega)$ is a nondegenerate eigenvalue, and we delete one equation from the system of equations (22). One of the unknowns may be put equal to anything, and the deleted system of equations is solved from the $N(\omega) - 1$ unknowns. This solution is inserted into the deleted equation and compared with the corresponding right-hand side. This gives a test on consistency and round-off errors.

Clearly, the system of equations (22) are not over-determined. The coefficients C_k in expansion (14) of Ψ_0 demonstrate the linear dependence among the rows of A_{kl}:

$$\sum_{k=1}^{N(\omega)} A_{lk} C_k = \langle U_l \mid H_0 - E_0(\omega) \mid \sum_{k=1}^{N(\omega)} C_k U_k \rangle$$

TABLE I. Results of variational calculations of the unperturbed energy of the $2\,^3P$ level and expectation values of potential and kinetic energies, in atomic units.

ω	$N(\omega)$	E_0	$\frac{1}{2}E^{(1)} = \frac{1}{2}\langle V \rangle$	$E_1^{(2)} = \langle T \rangle$
1	4	-2.129 471 787 9	-2.155 799 276 5	2.182 126 765 0
2	10	-2.132 678 402 0	-2.134 972 042 3	2.137 265 682 6
3	20	-2.133 085 039 2	-2.133 033 796 7	2.132 982 554 0
4	35	-2.133 140 222 3	-2.133 102 833 5	2.133 065 444 7
5	56	-2.133 157 595 1	-2.133 138 930 5	2.133 120 265 9
6	84	-2.133 162 289	-2.133 155 71	2.133 149 13
7	120	-2.133 163 594	-2.133 161 25	2.133 158 91
8	165	-2.133 163 983	-2.133 163 1	2.133 162 26
Extrapolated		-2.133 164 18(4)	-2.133 164 3(6)	2.133 164 4(9)

$$= \langle U_l \mid H_0 - E_0 \mid \Psi_0 \rangle$$

$$= 0 \quad \text{for } l = 1, 2, \ldots, N(\omega) .$$

The same relation holds for the right-hand side:

$$\sum_{k=1}^{N(\omega)} b_k^{(i)} C_k = \langle \sum_{k=1}^{N(\omega)} C_k U_k \mid H_1^{(i)} - E_1^{(i)} \mid \Psi_0 \rangle$$

$$= \langle \Psi_0 \mid H_1^{(i)} \mid \Psi_0 \rangle - E_1^{(i)} \langle \Psi_0 \mid \Psi_0 \rangle = 0$$

because of (7).

Theoretically, any one of the equations in (22) may be deleted. But the most important term in the expansion (14) for Ψ_0 is the first one, with $l = m = n = 0$, corresponding to the leading $(1s\,2p)$ term in a configuration expansion. As a practical matter, we put $X_n^{(i)} = 0$ when we delete the nth equation. The truncated matrix obtained by deleting the first row and column of A_{kl} is less close to being singular (is presumably better conditioned) than the one obtained by deleting the nth column and row of A_{kl} with $n > 1$. At higher dimensions $N(\omega)$ this may be important.

Tables I and II present the results in atomic units. All the computations reported in this work were done on a CDC-6600 computer in single-precision arithmetic (48 binary bits corresponding to slightly more than 14 decimals). When $X_2^{(i)}$, $X_3^{(i)}$, ..., $X_{N(\omega)}^{(i)}$ and $X_1^{(i)} = 0$ were inserted into the left-hand side of the first equation of (22) and compared with the right-hand side $b_1^{(i)}$, the numbers agreed to as many or more digits than the ones quoted for the results of Tables I and II. The iterative procedure for obtaining Ψ_0 was stopped when the difference between the eigenvalues calculated for two successive iterations were less than a certain prescribed ϵ in magnitude. For $1 \le \omega \le 5$ we used $\epsilon = 10^{-11}$, but for $\omega = 6, 7$, and 8, ϵ had to be increased to 10^{-10}. This does of course not imply that the elements C_n of the eigenvector are converged to anywhere near this accuracy, since the variational principle gives an eigenvalue one order better than the eigenvector, roughly speaking. We therefore iterated once more to obtain a slightly different wave function; the computations of Table

I were done for these two sets of wave functions. The results agreed to the digits quoted. The second-order energies $E_2^{(i,j)}$ were calculated by the two methods of Eq. (26) for both wave functions. The results using the two different methods (four in the case of $E_2^{(1,2)}$) calculated with the same wave function were in slightly better agreement (one more digit for $\omega = 6, 7,$ and 8) than the results calculated by the same method using different wave functions, for both methods.

The extrapolated results are obtained by methods discussed in the Sec. V. The extrapolated E_0 may be compared with Schwartz's best result of $-2.133 164 190 8$.[10] Relations (19) are well satisfied by the extrapolated results. Notice that the relations of the second-order energies among themselves are satisfied (to within round-off errors) for every value of ω. This is why we have one and not four columns in Table II, whereas the relation involving E_0 and the first-order energies are only obeyed accurately by the extrapolated result. This is obvious if we look at the usual sum for second-order energies, using a sum over a complete set of quantum states. For any term in the infinite sum there are the following relations for the numerators:

$$\langle 0 \mid T \mid n \rangle \langle n \mid V \mid 0 \rangle = \langle 0 \mid H_0 - V \mid n \rangle$$

$$= - \mid \langle 0 \mid V \mid n \rangle \mid^2 = - \mid \langle 0 \mid T \mid n \rangle \mid^2 ,$$

since $\mid n \rangle$ is an eigenstate of H_0, and $\mid n \rangle \ne \mid 0 \rangle$.

These results gives us some confidence that we have a sensible algorithm for computing second-order energies.

V. METHOD OF EXTRAPOLATION

Schwartz[26] has developed a method for estimating convergence rates of variational calculations based on an analogy with the problem of fitting a given function with a finite number of functions from an orthonormal basis. From this we expect the differences between the computed energies for suc-

TABLE II. Second-order perturbation energies from perturbation by the potential and kinetic energies, in atomic units.

ω	$E_2^{(1,1)} = E_2^{(2,2)} = -E_2^{(1,2)} = -E_2^{(2,1)}$
1	-1.801 314 478 0
2	-2.088 199 826 3
3	-2.128 536 110 3
4	-2.132 450 237 2
5	-2.132 976 961 2
6	-2.133 092 2
7	-2.133 137 4
8	-2.133 153 9
Extrapolated	$E_2^{(1,1)} = E_2^{(2,2)} = -E_2^{(1,2)} = 2.133\ 165(2)$

cessive variational calculations, labeled by ω, to be proportional to either α^ω or ω^{-p} ($|\alpha| < 1, p > 1$), called the fast or slow convergence rates, respectively. The unperturbed energies E_0 as well as the perturbations $E_1^{(i)}$ and $E_2^{(i,j)}$ should exhibit this behavior, qualitatively at least. Singularities in the total Hamiltonian will show up in slow convergence rates, unless the trial functions also have some (milder) singularities. We shall merely try to determine p or α empirically from the computed energies.

If the trial functions are good in the sense that they have the singularities of the wave functions (perturbed and unperturbed) built into them, one expects the fast convergence rate. However, even in the case of variational calculation of the unperturbed wave function ψ_0 for the $2\,^3P$ state, using the standard basis (13), the convergence rate will ultimately (for large ω) be slow because of a weak logarithmic singularity in the "exact" wave function when $r_1 \to 0$ and $r_2 \to 0$ simultaneously, the so-called Fock singularity.[27] The advantage of using additional trial functions proportional to $(r_1 + r_2)^{1/2}$ (Ref. 11) is that these approximate the Fock terms.

In the extrapolations in this work we try to fit the data to both the fast and slow rates. In the former case the ultimate values of α are guessed from the three or four last computed values of α; the ratio between successive differences between consecutively calculated energies. If Ω is the last value of ω for which the calculations are done, then the extrapolation is

$$(E_\Omega - E_{\Omega-1})[\alpha/(1-\alpha)] \qquad (27)$$

which is added to the last computed energy E_Ω; the uncertainty in α will give an uncertainty in the extrapolation. In the latter case the logarithm of differences between consecutively calculated energies, $\log |E_\omega - E_{\omega-1}|$, is plotted versus $\log \omega$, and we try to fit the points with a straight line with more emphasis on the points with higher values of ω; the success of the fit gives an indication of the usefulness of this extrapolation method. If the slope of the line is p, the extrapolation is

$$(E_\Omega - E_{\Omega-1})F_\Omega^+(p) ,$$

where

$$F_\Omega^+(p) = \sum_{n=1}^\infty \left(\frac{\Omega}{\Omega+n}\right)^p$$

$$\approx \frac{\Omega}{p-1}\,\frac{1}{2} + \frac{p}{12\Omega} - \frac{p(p+1)(p+2)}{720\,\Omega^3} \qquad (28)$$

when the sequence of calculated differences is monotonous. When the differences alternate in sign we have

$$F_\Omega^-(p) = \sum_{n=1}^\infty (-1)^n \left(\frac{\Omega}{\Omega+n}\right)^p$$

$$\approx -\frac{1}{2} + \frac{p}{4\Omega} - \frac{p(p+1)(p+2)}{48\,\Omega^3} . \qquad (29)$$

The extrapolated results of Tables I and II (where the energies decreased or increased montonically with ω) are somewhere between the values obtained from the two schemes, but closer to the extrapolated value given by the slow convergence rate. The uncertainties have been taken as half the difference between the two extrapolations.

Each reader must judge the accuracy of the extrapolated result for himself since the schemes are rather heuristic. A good portion of human judgment goes into the final extrapolated values, especially in the assignment of uncertainties. But we believe that a safe upper bound on the uncertainty is the extrapolated increment itself, i.e., the difference between the last calculated and the extrapolated energies.

VI. SECOND-ORDER ENERGIES WITH INTERMEDIATE ^3P STATES USING STANDARD BASIS

In atomic units the Breit-operators relevant for this work are

$$H_1^{(1)} = \frac{1}{4}\alpha^2 Z \left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right) \cdot \left(\frac{\vec{r}_1 \times \vec{p}_1}{r_1^3} + \frac{\vec{r}_2 \times \vec{p}_2}{r_2^3}\right) , \qquad (30)$$

$$H_1^{(2)} = -\frac{3}{4}\alpha^2 \left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right) \cdot \left(\frac{(\vec{r}_1 - \vec{r}_2)\times(\vec{p}_1 - \vec{p}_2)}{r_{12}^3}\right) , \qquad (31)$$

$$H_1^{(3)} = \frac{1}{4}\alpha^2 \frac{1}{r_{12}^3}\left(\vec{\sigma}_1\cdot\vec{\sigma}_2 - \frac{3(\vec{\sigma}_1\cdot\vec{r}_{12})(\vec{\sigma}_2\cdot\vec{r}_{12})}{r_{12}^2}\right) , \qquad (32)$$

$$H_1^{(4)} = -\frac{1}{2}\alpha^2\frac{1}{r_{12}}\left[\vec{p}_1\cdot\vec{p}_2 + \frac{(\vec{r}_{12}\cdot\vec{p}_1)(\vec{r}_{12}\cdot\vec{p}_2)}{r_{12}^2}\right] , \qquad (33)$$

$$H_1^{(5)} = -\frac{1}{8}\alpha^2(p_1^4 + p_2^4) , \qquad (34)$$

$$H_1^{(6)} = \frac{1}{2}Z\pi\alpha^2[\delta^{(3)}(\vec{r}_1) + \delta^{(3)}(\vec{r}_2)] , \qquad (35)$$

and the operator correcting for the finite mass M of the He^4 nucleus is, in atomic units,

$$H_1^{(7)} = \frac{m}{M}\vec{p}_1\cdot\vec{p}_2 . \qquad (36)$$

Here m is the (reduced) electron mass, $m/M \approx 1.36 \times 10^{-4}$, so the operator (36) is somewhat more important than the Breit operators since $\alpha^2 = 0.53 \times 10^{-4}$. The operator $H_1^{(1)}$ is the coupling between the spin and the orbit of the same electron, for both electrons ($Z = 2$), $H_1^{(2)}$ is the coupling between the spin of one electron and the orbit of the other, and $H_1^{(3)}$ is the spin-spin (or dipole-dipole) interaction. These are the only spin-dependent Breit operators.

$H_1^{(4)}$ is due to the retarded interaction between the orbits of the two electrons, $H_1^{(5)}$ is a correction coming from the relativistic variation of the electron mass with velocity, and the contact interaction $H_1^{(6)}$ is a term characteristic of Dirac theory. There has been some confusion about this operator[13]; the

one given by Bethe and Salpeter[28] is not Hermitian. The operator $H_1^{(6)}$ has been obtained in the form (35) by Itoh[13] and Kim.[14] In this work we shall only calculate contributions when the perturbation wave functions $\Psi_1^{(i)}$ have the same symmetry as Ψ_0, i.e., from intermediate triplet P states with odd parity. Therefore, some terms in the spin-orbit operators proportional to $\vec{\sigma}_1 - \vec{\sigma}_2$ which have vanishing matrix elements between states of the same multiplicity have been left out. From the operators $H_1^{(3)}$ and $H_1^{(6)}$ we have left out terms proportional to $\delta^{(3)}(\vec{r}_{12})$ whose matrix elements between standard terms (13) vanish.

The spin-orbit operator (including the term that we dropped) is a contraction of an irreducible spherical tensor operator of rank one in spin space and a similar operator in ordinary space. Acting on a triplet P state it will then give a mixture of triplet P, triplet D and also singlet P, singlet D. There can be no higher multiplicities since two electron spins can only give triplet and singlet. The spin-orbit interaction has even parity, so it does not change parity, therefore there are no S states; these would have to have the odd parity of Ψ_0, and it is impossible to construct an odd scalar from $\vec{r}_1$ and $\vec{r}_2$. The spin-spin operator $H_1^{(3)}$ is a contraction of a spin operator of rank two and an operator in ordinary space of the same rank. Acting on Ψ_0 it will then give a mixture of intermediate P, D, and F states, all triplets with odd parity. The second-order perturbation energies that we do not attempt to calculate in this work are thus second-order spin-orbit energies from intermediate ^1D, ^1P, and ^3D states, second-order spin-spin energies from intermediate ^3D and ^3F states, and a mixed second-order contribution from the spin-orbit and spin-spin interactions with intermediate ^3D states.

The details of the calculations of the matrix elements

$$\langle U_{l'm'n'} | H_1^{(i)} | U_{lmn} \rangle , \quad i = 1, 2, \ldots, 7$$

where U_{lmn} is given by (13), are described in Appendix B, and the calculation of the necessary integrals is discussed in Appendix A. In Table III we give the expectation values of the seven operators, using the wave functions ψ_0 (14) for $\omega = 1, 2, \ldots, 8$. The units are chosen for comparison with the results of Schwartz[10] and Schiff et al.[25]. These results are for "stretched" states where $J = m_J = 2$. As in Sec. IV, all calculations were done with two sets of slightly different wave functions ψ_0, and the results agreed to the digits quoted. For $\omega \leq 4$ there was complete agreement for all 11 digits with which we had the computer print the results. Careful extrapolations according to the schemes of Sec. V has been made, the assigned errors come mostly from the uncertainties in the values of α or p used in formulas (27)–(29); this is probably too optimistic. The ex-

TABLE III. Expectation values of the operators (37)–(43) using Hylleraas expansions (18) for the wave functions.

ω	$E_1^{(1)}(\tfrac{1}{2}\alpha^2\mathfrak{R})$	$E_1^{(2)}(\tfrac{1}{2}\alpha^2\mathfrak{R})$	$E_1^{(3)}(\tfrac{1}{2}\alpha^2\mathfrak{R})$	$E_1^{(4)}(2\alpha^2\mathfrak{R})$	$E_1^{(5)}(2\alpha^2\mathfrak{R})$	$E_1^{(6)}(2\alpha^2\mathfrak{R})$	$E_1^{(7)}[2(m/M)\mathfrak{R}]$
1	0.136 215 710 56	−0.218 277 449 69	0.019 652 745 588	0.034 490 724 822	−9.650 474 2823	7.802 284 9193	−0.058 229 558 253
2	0.131 125 093 81	−0.201 776 410 02	0.018 015 107 575	0.032 904 898 326	−9.974 203 3112	7.945 181 0162	−0.059 299 556 963
3	0.134 790 079 01	−0.203 087 634 20	0.017 932 223 852	0.034 113 074 489	−9.901 226 0173	7.905 371 7914	−0.061 960 762 81
4	0.136 881 098 90	−0.204 591 378 83	0.017 982 384 057	0.034 672 686 84	−9.915 990 795 6	7.912 170 1450	−0.063 377 555 21
5	0.137 897 9722	−0.205 354 114 7	0.018 001 120 12	0.034 940 446 83	−9.910 076 60	7.908 943 679	−0.064 191 432 30
6	0.138 340 7	−0.205 676 3	0.018 009 43	0.035 035 69	−9.911 83	7.909 714	−0.064 463 46
7	0.138 519 5	−0.205 803 67	0.018 012 740	0.035 065 736	−9.911 526 58	7.909 518 9	−0.064 535 66
8	0.138 593 4	−0.205 860 0	0.018 014 27	0.035 075 96	−9.911 905	7.909 689	−0.064 562 9
∞	0.138 64(1)	−0.205 91(1)	0.018 016(1)	0.035 082(2)	−9.911 80(5)	7.909 64(1)	−0.064 580(5)

pectation values are in very satisfactory agreement with the results of Schwarz[10] and Schiff *et al.*[25] Notice that the sequences of energies are monotonic with ω for all but the lowest values of ω, except for $E_1^{(5)}$ and $E_1^{(6)}$, where the differences alternate in sign.

The second-order perturbation energies $E_2^{(i,j)}$ are calculated by the methods described in detail in Secs. II and IV. The spin-dependent results are given in Table IV; all values are for perturbations on the stretched state. Since the spin-independent second-order energies can be done with no extra effort (and very little more computer time), we also did these calculations and report the results in Appendix C. Each energy was computed by the two different methods (26), and this was done with the two slightly different wave functions Ψ_0. There are thus four numbers to compare for the unmixed and eight for the mixed second-order energies. The discrepancies between the eight (or four) numbers increases with ω, indicating accumulating round-off errors. One of the reasons for this may be that the matrix A_{lk} in (22) with the first row and column deleted gets close to being singular as ω increases, as mentioned in Sec. IV. This affects both Ψ_0 and $\Psi_1^{(i)}$ since the matrix A_{lk} enters the eigenvalue problem for Ψ_0. Generally, the discrepancy between results calculated the same way with the two different Ψ_0's was slightly larger, usually one more digit, than the disagreement between the values calculated by the two different methods, using the same Ψ_0. When the solutions $X_2^{(i)}$, $X_3^{(i)}$, ..., $X_{N(\omega)}^{(i)}$ were inserted into the left-hand side of (22) and compared with the right-hand side $b_1^{(i)}$, the numbers agreed to as many or more digits than the ones in Table IV, just as in Sec. IV. The loss of accuracy is rather different for the various second-order energies. It is most pronounced when the spin-dependent operators are mixed with $H_1^{(5)}$ and $H_1^{(6)}$. In these cases, for the highest values of ω, we have quoted numbers with uncertainties, this being half the difference between the smallest and largest among the eight values obtained for the second-order energies.

Careful extrapolations have been done, using both (27), denoted F for fast, and (28) or (29), denoted S for slow. In the former case α, the ratio between successive differences, has been assigned a value with fairly generous uncertainties. Whenever α increased steadily with ω (there was no case with monotonic decrease of α), we guessed at an extrapolated value of α. In the latter case the absolute value of the successive differences was plotted versus ω on log-log paper, and several straight lines were fitted to the points, giving the slope p with some uncertainty, to be used in (28) when all ratios α are positive or in (29) when all ratios of successive differences are negative. When the spin-dependent operators are mixed with themselves and with

TABLE IV. Second-order spin-dependent perturbation energies, using only standard terms (18) in the expansion for $\psi_1^{(i)}$ ($i = 1, 2, \ldots, 7$).

ω	$E_2^{(1,1)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(1,2)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(3,3)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(1,2)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(1,3)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(1,4)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(1,5)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(1,6)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(1,7)}(\frac{1}{2}\alpha^2\mathfrak{R})m/M$
1	−0.246 939 977 79	−0.606 520 192 22	−0.003 914 987 988 6	0.375 263 457 93	0.029 729 889 761	−0.064 385 508 470	−1.352 917 820 9	0.832 024 229 82	0.088 292 460 19
2	−0.365 389 076 52	−0.796 511 077 86	−0.004 868 968 719 5	0.511 063 002 22	0.039 027 567 208	−0.096 387 812 967	0.033 575 9747	0.122 374 672 0	0.160 069 879 02
3	−0.442 532 341 44	−0.892 241 821 97	−0.005 258 842 720	0.579 233 469 60	0.043 180 481 13	−0.113 398 137 93	−0.195 349 854 0	0.263 052 759 2	0.187 985 961 96
4	−0.489 473 765 4	−0.950 705 901 7	−0.005 438 701 801	0.614 765 999 2	0.045 005 653 53	−0.127 737 003 0	−0.115 321 34	0.236 553 35	0.205 644 018
5	−0.522 677 88	−0.990 380 77	−0.005 554 941 3	0.636 515 46	0.045 980 42	−0.128 466 35	−0.141 174	0.259 488	0.219 018 34
6	−0.545 878	−1.017 182	−0.005 636 5	0.649 20	0.046 520	−0.131 587 4	−0.131 8	0.261 25	0.225 658
7	−0.5622	−1.036 32	−0.005 697	0.6570	0.046 84	−0.133 186	−0.127 0(5)	0.262 9(3)	0.228 29
8	−0.5747	−1.0509	−0.005 746	0.6617	0.047 05	−0.134 116	−0.105 2(6)	0.255 7(3)	0.230 35
	−0.61(1) F	−1.10(3) F	−0.005 9(3) F	0.672(5) F	−0.047 3(2) F	−0.135 4(3) F			0.240(8) F
	−0.67(3) S	−1.15(5) S	−0.006 1(1) S	0.681(5) S	−0.047 6(1) S	−0.136 0(5) S	−0.10(5)	0.26(3)	0.238(5) S

ω	$E_2^{(2,3)}(\frac{1}{2}\alpha^2\mathfrak{R})\frac{1}{4}\alpha^2$	$E_2^{(2,4)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(2,5)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(2,6)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(2,7)}(\frac{1}{2}\alpha^2\mathfrak{R})m/M$	$E_2^{(3,4)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(3,5)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(3,6)}(\frac{1}{2}\alpha^2\mathfrak{R})\alpha^2$	$E_2^{(3,7)}(\frac{1}{2}\alpha^2\mathfrak{R})m/M$
1	0.048 646 059 033	0.108 392 432 11	2.102 026 9660	−1.248 300 545 9	−0.169 152 046 28	−0.008 741 807 952	−0.135 460 823 01	0.079 731 206 176	0.013 890 400 158
2	0.061 924 185 65	0.145 649 986 24	0.293 942 2327	−0.009 042 191 6	−0.235 875 173 58	−0.011 210 409 140	0.025 674 811 26	−0.003 859 000 32	0.018 025 837 945
3	0.067 859 016 36	0.164 060 352 69	0.295 591 4804	−0.321 767 155 4	−0.271 576 207 12	−0.012 264 960 508	0.000 925 262 88	0.009 283 318 774	0.020 086 284 654
4	0.071 008 825 84	0.174 209 645 4	0.044 857 98	−0.206 227 866	−0.292 059 28	−0.012 751 258 04	0.007 202 628	0.006 632 136	0.020 936 916 61
5	0.073 049 241	0.179 989 96	0.144 581 3	−0.262 353 6	−0.306 044 85	−0.012 982 926	0.006 856 39	0.007 082 55	0.021 347 172
6	0.074 454	0.182 862	0.087 70(4)	−0.2373	−0.312 580	−0.013 091 0	0.007 25(3)	0.006 99	0.021 498
7	0.075 49	0.184 252	0.121 6(3)	−0.255 6(2)	−0.315 64	−0.013 144 2	0.006 83(5)	0.007 35(3)	0.021 572
8	0.076 29	0.185 02	0.102 1(4)	−0.248 1(2)	−0.317 74	−0.013 171	0.006 73(6)	0.007 45(3)	0.021 604
	0.079(1) F	0.185 9(3) F	0.109 0(6) F	−0.250 8(9) F	−0.323(3) F	−0.013 198(6) F			0.021 63(5) F
8	0.082(1) S	0.186 4(3) S	0.109 7(1) S	−0.251 3(1) S	−0.325(5) S	−0.013 22(2) S	0.006 7(5)	0.007 5(5)	0.0217(1) S

$H_1^{(4)}$ and $H_1^{(7)}$, the second-order energies are all monotonic with ω as were the first-order energies $E_1^{(i)}$ ($i = 1, 2, 3, 4$, and 7). The quantities $E_2^{(2,5)}$ and $E_2^{(2,6)}$ oscillate in a very regular manner with increasing ω, permitting a rather accurate extrapolation. This may be accidental since $E_2^{(1,5)}$, $E_2^{(1,6)}$, $E_2^{(3,5)}$, and $E_2^{(3,6)}$ behave quite erratically as ω increases. In these four cases extrapolation methods cannot be justified, so we have just guessed at the final values.

A general feature of these results is that slow or fuzzy convergence is associated with sharp loss of numerical accuracy with increasing ω, as well as with enhanced sensitivity to a small variation in Ψ_0, and that the seriousness of these diseases for a particular $E_2^{(i,j)}$ is determined by how singular the operators $H_1^{(i)}$ and $H_1^{(j)}$ are. Whenever $H_1^{(5)}$ or $H_2^{(6)}$ are involved neither the first-order nor the second-order energies are monotonic with ω, except for $E_2^{(5,5)}$, $E_2^{(6,6)}$, and $E_2^{(5,6)}$. That these two operators should cause similar behavior is reasonable since both yield δ functions (of $\vec{r}_1$ and $\vec{r}_2$) when acting on Ψ_0. The other operators all give pole-type singularities at the nucleus ($r_1 = 0$ or $r_2 = 0$) or when the electrons come together ($r_{12} = 0$). For $(H_0 - E_0)\Psi_1^{(i)}$ to give δ functions we need terms proportional to $\vec{r}_1/r_{12}$ or $\vec{r}_2/r_1$ in the expansion of $\Psi_1^{(i)}$, but to reproduce the poles one only needs terms proportional to $\vec{r}_1/r_1$ or $\vec{r}_2/r_2$ or $\vec{r}_{12}/r_{12}$ [corresponding to an expansion like (19) starting with $l = -1$ for $\Psi_1^{(i)}$], so it is not surprising that the operators $H_1^{(5)}$ and $H_1^{(6)}$ give perturbation energies whose behavior as ω increases is quite distinct from that of the other five operators. It seems as if the mixed second-order energies, whose convergence is controlled by the poles at $r_1 = 0$ (or $r_2 = 0$) and $r_{12} = 0$ are better converged than the unmixed ones who are controlled by one kind of singularity only. One might expect that the convergence rates determined by the pole at $r_{12} = 0$ would be faster than the ones associated with the poles at $r_1 = 0$ or $r_2 = 0$, since both $\Psi_1^{(i)}$ and Ψ_0 vanish when $r_{12} = 0$ (because of antisymmetry), and thus that $E_2^{(1,1)}$ should converge more slowly than $E_2^{(2,2)}$ and $E_2^{(3,3)}$, although this does not seem to be the case for our values of ω.

The spin-dependent operators displace the three fine-structure levels. In first-order perturbation theory the displacements are

$$(E_1)_J = (E_1^{(1)} + E_1^{(2)})f(J) + E_1^{(3)}g(J) ,$$

where, for this particular case,

$$f(J) = \frac{J(J+1) - 4}{2} , \qquad g(J) = \frac{120(-1)^J}{(3+J)!(2-J)!} ,$$

which follows from the Wigner-Eckhart theorem.[29] Here the expectation values $E_1^{(i)}$, $i = 1, 2, 3$ have been taken for the "stretched" state where $J = m_J = 2$, so that $f(2) = g(2) = 1$. In second-order perturbation

theory the J dependence of the corrections are given by

$$(E_2^{(i,j)})_J = \sum_n{}' \frac{[\langle 0|H_1^{(i)}|n\rangle]_J[\langle n|H_1^{(j)}|0\rangle]_J}{E_0 - E_n} , \quad (37)$$

where the matrix elements $[\langle 0|H_1^{(i)}|n\rangle]_J$ are between triplet P states, hence their J dependence is precisely that of the first-order perturbations. These matrix elements are of course diagonal in J since $H_1^{(i)}$ are scalar operators. Since E_0 and E_n are unperturbed J-independent energies, we obtain the second-order displacements

$$(E_2)_J = [f(J)]^2(E_2^{(1,1)} + E_2^{(2,2)} + 2E_2^{(1,2)})$$

$$+ 2f(J)g(J)\sum_{i=1}^2 E^{(i,3)} + [G(J)]^2 E_2^{(3,3)}$$

$$+ 2f(J)\sum_{i=1}^2 \sum_{j=4}^7 E_2^{(i,j)} + 2g(J)\sum_{j=4}^7 E_2^{(3,j)} ,$$

where $E_2^{(i,j)}$ refers to the quantities of Table IV [they are the corrections given by (44) with $J = 2$]. The fine-structure interval $\nu_{01} = (E_1)_0 - (E_1)_1$ is adjusted by an amount $\Delta\nu_{01} = (E_2)_0 - (E_2)_1$:

$$\Delta\nu_{01} = \tfrac{1}{2}\alpha^2\,\mathfrak{R}\,\{\tfrac{1}{4}\alpha^2[3(E_2^{(1,1)} + E_2^{(2,2)} + 2E_2^{(1,2)})$$

$$- 50(E_2^{(1,3)} + E_2^{(2,3)}) + 75E_2^{(3,3)}] - 2\alpha^2(E_2^{(1,4)} + E_2^{(2,4)})$$

$$+ E_2^{(1,5)} + E_2^{(2,5)} + E_2^{(1,6)} + E_2^{(2,6)}) + 30\,\alpha^2(E_2^{(3,4)} + E_2^{(3,5)})$$

$$+ E_2^{(3,6)}) + 2(m/M)(-E_2^{(1,7)} - E_2^{(2,7)} + 15E_2^{(3,7)})\}$$

$$(38)$$

and there are similar formulas for $\Delta\nu_{12}$ and $\Delta\nu_{02}$. In Table V the two extrapolated results of Table IV are combined into single final values for the second-order energies. The uncertainties in the extrapolations are mostly products of human judgment (or

TABLE V. Contributions of the second-order energies of Table IV to the fine-structure intervals.

(i, j)	Final result for $E_2^{(i,j)}$ from Table IV	Contribution to $\Delta\nu_{0i}$ in 10^{-4} cm^{-1}	Contribution to $\Delta\nu_{12}$ in 10^{-4} cm^{-1}
(1, 1)	$-0.63(4)$	$-0.74(5)$	0
(2, 2)	$-1.12(5)$	$-1.31(6)$	0
(1, 2)	$0.677(5)$	$1.58(1)$	0
(1, 3)	$-0.0475(2)$	$0.924(4)$	$-0.1478(6)$
(2, 3)	$0.080(2)$	$-1.56(4)$	$0.249(6)$
(3, 3)	$-0.0060(3)$	$-0.175(9)$	$-0.056(3)$
(1, 4)	$-0.1356(5)$	$0.4218(16)$	$0.8437(31)$
(2, 4)	$0.1862(4)$	$-0.5793(12)$	$-1.159(2)$
(3, 4)	$-0.013\,20(2)$	$-0.6160(9)$	$0.2464(4)$
(1, 5)	$-0.10(5)$	$0.31(16)$	$0.62(31)$
(2, 5)	$0.1095(6)$	$-0.3407(19)$	$-0.6814(37)$
(1, 6)	$0.26(3)$	$-0.81(9)$	$-1.62(19)$
(2, 6)	$-0.2512(9)$	$0.7816(28)$	$1.563(6)$
(3, 5)	$0.0067(5)$	$0.31(2)$	$-0.125(9)$
(3, 6)	$0.0075(5)$	$0.35(2)$	$-0.140(9)$
(1, 7)	$0.239(5)$	$-1.90(4)$	$-3.80(8)$
(2, 7)	$-0.324(3)$	$2.58(2)$	$5.16(4)$
(3, 7)	$0.0216(1)$	$2.58(1)$	$-1.031(5)$
Experimental values		$9879.121(12)$	$764.2606(17)$

prejudice). The contributions of these 18 corrections to the fine-structure intervals ν_{01} and ν_{12} in wave numbers are computed from (45) and the corresponding expression for $\Delta\nu_{12}$. The conversion factor $\alpha^2(\frac{1}{2}\alpha^2\Re) = 1.555\,671\,(9)\times10^{-4}$ cm^{-1} (6 ppm) has been obtained from Tables XXXII and XI of Ref. 4.

As seen from Table V, some of the second-order energies $E_2^{(i,j)}$ have an accuracy which is a good deal greater than that of the present experimental value for ν_{01} (good to about 2 ppm), but the situation as regards ν_{12} is not nearly so good. The results fall short of the desired accuracy, which is to surpass the precision of the experimental values. But they demonstrate that all second-order contributions are important and will have to be calculated to several significant figures before a determination of the fine-structure constant can be made from the measured values of ν_{01} and ν_{12}. Previously, only one second-order correction has been calculated, the mixing (by the spin-orbit coupling) with the nearby $2\,^1P$ state, Pekeris et al.[30] find that this shifts the $J = 1$ level 1.58×10^{-4} cm^{-1} downwards, of the same order of magnitude as our results.

One can try two paths to achieve better accuracy for the various $E_2^{(i,j)}$. One possibility is to go on to higher values of ω, using just the standard basis as we have done here. In view of the rather sharp loss of accuracy for some of the $E_2^{(i,j)}$ as ω increases, one would probably have to use double-precision arithmetic for $\omega \gtrsim 10$, say. Although the calculations reported here were done in a matter of minutes on a CDC-6600 computer it was decided not to go on to higher values of ω, since the computer time requirements would increase drastically. The second alternative is to make the trial functions for $\psi_1^{(i)}$ more flexible. In a future paper we shall see some examples of how this leads to increased accuracy.

APPENDIX A: INTEGRALS

We describe here the evaluation of the many integrals needed for the calculation of the matrix elements of the operators between functions used for the variational expansions. Most of the tricks have already been used by Schwartz[10] and Hambro.[23]

The majority of the matrix elements of the operators $H_0, H_1^{(1)}, \ldots, H_1^{(7)}$ are expressed in terms of the four basic types of integrals:

$$A(L, M, N) = \int \frac{dv_1}{4\pi} \int \frac{dv_2}{4\pi} \, e^{-ar_1} e^{-br_2} r_1^{M-2} r_2^{N-2} r_{12}^{L-2} \, ,$$

$$B(L, M, N) = \int \frac{dv_1}{4\pi} \int \frac{dv_2}{4\pi}$$
$$\times \, e^{-ar_1} e^{-br_2} r_1^{M-2} r_2^{N-2} r_{12}^{L-2} \cos\theta_{12} \, .$$

There are two kinds of A and B integrals, the direct ones for which $a = \kappa\sigma$, $b = \kappa$, called $A_{DI}(L, M, N)$ and $B_{DI}(L, M, N)$ and the exchange ones for which $a = b = \frac{1}{2}\kappa(1 + \sigma)$, called $A_{EX}(L, M, N)$ and $B_{EX}(L, M, N)$. The following recursion formulas are used:

$$A(L, M, N) = A(L - 2, M + 2, N) + A(L - 2, M, N + 2)$$
$$- 2B(L - 2, M + 1, N + 1) \, , \quad (A1)$$

which follow from

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}, \quad (A2)$$

and

$$B(L, M, N) = [(L - 2)/(L + 2)][B(L - 2, M + 2, N)$$
$$+ B(L - 2, M, N + 2) - 2A(L - 2, M + 1, N + 1)] \, , \quad (A3)$$

which follow from (A2) and

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \sin^2\theta_{12} r_{12}^L$$
$$= \frac{-2}{L + 2} \int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \cos\theta_{12} \frac{r_{12}^{L+2}}{r_1 r_2} \, . \quad (A4)$$

This identity is proved by one partial integration; take $\vec{r}_1$ as fixed along the z axis, then $\theta_{12} = \theta_2 \equiv \theta$ and

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} F(\theta_{12}) = \frac{1}{2} \int_0^\pi d\theta \, \sin\theta \, F(\theta) \, .$$

The recursive calculation is started by

$$B(2, M, N) = 0, \quad A(2, M, N) = \frac{M! \, N!}{a^{M+1} b^{N+1}} \, ,$$

$$A(1, M, N) = F(M + 1, N; a, b) + F(N + 1, M; b, a) \, ,$$
$$(A5)$$

$$B(1, M, N) = \frac{1}{3} [F(M + 2, N - 1; a, b)$$
$$+ F(N + 2, M - 1; b, a)] \, , \quad (A6)$$

where the F integrals are defined by

$$F(M, N; \alpha, \beta) = \int_0^\infty dr \, e^{-\alpha r} r^{M-1} \int_r^\infty ds \, e^{-\beta s} s^{N-1} \, .$$

There are three kinds of F integrals; for the computation of the direct A and B integrals we need F integrals with $\alpha = \kappa$, $\beta = \kappa\sigma$ and $\alpha = \kappa\sigma$, $\beta = \kappa$ and for the exchange integrals we need the F integrals for $\alpha = \beta = \frac{1}{2}\kappa(1 + \sigma)$. It is easy to calculate the F integrals:

$$F(M, 1; \alpha, \beta) = \frac{1}{\beta} \frac{(M - 1)!}{(\alpha + \beta)^M} \, ,$$

$$F(M, N; \alpha, \beta) = \frac{(M + N - 2)!}{\beta(\alpha + \beta)^{M+N-1}} + \frac{N - 1}{\beta} F(M, N - 1; \alpha, \beta)$$

follow after one partial integration in s. Equations (A5) and (A6) follow from

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \frac{1}{r_{12}} = \frac{1}{r_>}, \qquad \int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \frac{\cos\theta_{12}}{r_{12}} = \frac{r_<}{3r_>^2},$$

where $r_>(r_<)$ is the greater (smaller) of r_1 and r_2.

These recursion schemes give the A integrals for $L \geqslant 1$, $M \geqslant 1$, $N \geqslant 1$ and the B integrals for $L \geqslant 1$, $M \geqslant 2$, $N \geqslant 2$. The schemes are all safe in the sense that there are no substantial loss of accuracy due to subtraction of almost equal quantities. For $L > 2$ the B integrals are all negative because the dominant contribution to B integrals with a positive power of r_{12} comes from large values of r_{12} when $\cos\theta_{12}$ is negative. So for $L \geqslant 4$ the recursion formulas (A1) and (A3) are safe. By looking at the actual numbers involved one can convince oneself that there is no important loss of accuracy when $L = 3$. These integrals are sufficient for the calculation of matrix elements of H_0, $H_1^{(6)}$, and $H_1^{(7)}$ in the standard basis.

The integrals

$$F_L(M,N;\alpha\beta) = \int_0^\infty dr\, e^{-\alpha r} r^{M-1} \int_r^\infty ds\, e^{-\beta s} s^{N-1} \ln\frac{s+r}{s-r}$$

for $\alpha = \kappa$, $\beta = \kappa\sigma$ and $\alpha = \kappa\sigma$, $\beta = \kappa$, and $\alpha = \beta = \frac{1}{2}\kappa(1+\sigma)$ are also required. Substituting $r = yx$ and $s = y$ we get

$$F_L(M,N;\alpha,\beta)$$
$$= \int_0^1 dx\, x^{M-1} \ln\frac{1+x}{1-x} \int_0^\infty dy\, y^{M+N-1} e^{-(\alpha x+\beta)y}$$
$$= \frac{(M+N-1)!}{\alpha^{M+N}} \int_0^1 dx\, \frac{x^{M-1}\ln[(1+x)/(1-x)]}{(x+\beta/\alpha)^{M+N}}.$$

Substituting $x = (1-u)/(1+u)$ we obtain

$$F_L(M,N;\alpha,\beta)$$
$$= \frac{(M+N-1)!}{\alpha^{M+N}} \int_0^1 2\,du\, \frac{(1-u)^{M-1}(1+u)^{N-1}\ln(1/u)}{[1-u+(\beta/\alpha)(1+u)]^{M+N-2}}.$$

To avoid dangerous recursion schemes we compute the integrals along $M+N = \text{const}$ and use the backwards recursion formula

$$F_L(M,N;\alpha,\beta)$$
$$= \frac{\alpha F_L(M+1,N;\alpha,\beta) + \beta F_L(M,N+1;\alpha,\beta)}{M+N}. \qquad (A7)$$

For the actual calculation we must treat the three cases separately.

For $\alpha = \beta$, we have

$$F_L(M,N;\alpha,\beta) = \frac{(M+N-1)!}{\alpha^{M+N}} \sum_{J=1}^N \binom{N-1}{J-1} \frac{1}{2^{M+N-J}}$$
$$\times \int_0^1 du\, u^{J-1}(1-u)^{M+N-J-1}\ln\frac{1}{u},$$

where the expansion

$$(1+u)^{N-1} = \sum_{J=1}^N \binom{N-1}{J-1}(2u)^{J-1}(1-u)^{N-J}$$

has been used. Defining the integrals

$$J(M,N) = -\int_0^1 du\, u^{M-1}(1-u)^{N-1}\ln u$$
$$= -\frac{\partial}{\partial M}\int_0^1 du\, u^{M-1}(1-u)^{N-1} = -\frac{\partial}{\partial M}B(M,N),$$

where $B(M,N)$ is Euler's Beta-function, we have

$$J(M,N) = -\frac{\partial}{\partial M}\frac{\Gamma(M)\Gamma(N)}{\Gamma(M+N)}$$
$$= -\frac{\Gamma(M)\Gamma(N)}{\Gamma(M+N)}\left(\frac{\Gamma'(M)}{\Gamma(M)} - \frac{\Gamma'(M+N)}{\Gamma(M+N)}\right)$$
$$= -\frac{\Gamma(M)\Gamma(N)}{\Gamma(M+N)}\left[\left(\sum_{k=1}^{M-1}\frac{1}{k} - \gamma\right) - \left(\sum_{k=1}^{M+N-1}\frac{1}{k} - \gamma\right)\right]$$

where γ is Eulers constant.[31] Thus we have

$$J(M,N) = \frac{(M-1)!\,(N-1)!}{(M+N-1)!}$$
$$\times\left(\frac{1}{M} + \frac{1}{M+1} + \cdots + \frac{1}{M+N-1}\right)$$

and we obtain a closed expression,

$$F_L(M,N;c,c) = \frac{1}{c^{M+N}}\sum_{J=1}^N \frac{(N-1)!}{(N-J)!}(M+N-J-1)!$$
$$\times 2^J\left(\frac{1}{J} + \cdots + \frac{1}{M+N-1}\right),$$

where $c = k(1+\sigma)$.

For $\alpha = \kappa > \beta = \kappa\sigma$ and $\beta/\alpha = \sigma$, the expansion

$$\frac{1}{[1-u+\sigma(1+u)]^L}$$
$$= \frac{1}{(1+\sigma)^L}\left(1 + \sum_{k=1}^\infty \frac{B^k u^k}{k!} L(L+1)\cdots(L+k-1)\right)$$

is used where $B = (1-\sigma)/(1+\sigma) < 1$. This gives an infinite series for the integrals

$$F_L(M,N;\kappa,\kappa\sigma)$$
$$= \frac{1}{A^{M+N}}\sum_{k=0}^\infty\left(\sum_{J=1}^N F_J(J)F_{JK}(J,k)S_{KJ}(J,k)\right),$$

where $A = \kappa(1+\sigma)$ and

$$F_J(J) = 2^J(N-1)!\,(M+N-J-1)!/(N-J)!,$$
$$F_{JK}(J,k) = B^k J(J+1)\cdots(k+J-1)/k! \quad \text{for } k \geqslant 1,$$
$$F_{JK}(J,0) = 1,$$
$$S_{KJ}(J,k) = \frac{1}{k+J} + \cdots + \frac{1}{k+M+N-1}.$$

This looks complicated, but the formula lends itself to an efficient programming. The series is rapidly converging; in the program we truncate when the ratio of the kth term to the sum of the first $k-1$ terms falls below a certain ϵ (we used

$\epsilon = 10^{-10}$).

The third and last case is when $\alpha = \kappa\sigma < \beta = \kappa$ and $\beta/\alpha = 1/\sigma$; the appropriate expansion is then

$$\frac{1}{[1 - u + (1/\sigma)(1 + u)]^L}$$

$$= \left(\frac{\sigma}{2}\right)^L \left(1 + \sum_{k=1}^{\infty} \frac{B^k(1-u)^k}{k!} L(L+1)\cdots(L+k-1)\right),$$

where $B = \frac{1}{2}(1 - \sigma) < 1$. This gives an infinite series of the same form as the one for $F_L(M, N; \kappa, \kappa\sigma)$ but with $A = 2\kappa$ and

$$F_{JK}(J, k)$$

$$= B^K(M+N-J)\cdots(M+N-J+k-1)/k! \quad \text{for} \quad k \geq 1,$$

$$F_{JK}(J, 1) = 1, \quad S_{KJ}(J, k) = \frac{1}{J} + \cdots + \frac{1}{k+M+N-1},$$

and $F_J(J)$ is unchanged.

Armed with these F_L integrals we compute the $A(L, M, N)$ integrals with $L = 0$, $M \geq 1$, $N \geq 1$ and $B(L, M, N)$ integrals with $L = 0$, $M \geq 2$, $N \geq 2$:

$$A_{DI}(0, M, N) = \frac{1}{2}[F_L(M, N; \kappa\sigma, \kappa) + F_L(N, M; \kappa, \kappa\sigma)],$$

$$B_{DI}(0, M, N)$$

$$= \frac{1}{4}[F_L(M+1, N-1; \kappa\sigma, \kappa) + F_L(M-1, N+1; \kappa\sigma, \kappa)$$

$$+ F_L(N+1, M-1; \kappa, \kappa\sigma) + F_L(N-1, M+1; \kappa, \kappa\sigma)]$$

$$- \frac{1}{2}[F(M, N; \kappa\sigma, \kappa) + F(N, M; \kappa, \kappa\sigma)],$$

and there are similar formulas for $A_{EX}(0, M, N)$ and $B_{EX}(0, M, N)$.

We also require the A and B integrals for $M = 0$, $N \geq 1$ and $M \geq 1$, $N = 0$ when $L \geq 1$. To obtain these, one has to evaluate the integrals $F(M, N; \alpha, \beta)$ with $N = 0$ and $N = -1$. Once the integrals for $N = 0$ are found, the ones for $N = -1$ (and more negative values of N) are obtained from

$$F(M, -N; \alpha, \beta)$$

$$= \frac{(M-N-1)!}{N(\alpha+\beta)^{M-N}} - \frac{\beta}{N} F(M, -N+1; \alpha, \beta), \quad \text{(A8)}$$

which results from one partial integration. So we can calculate F integrals with negative N as long as $M - N \geq 1$ with this scheme. A recursion formula for $F(M, 0; \alpha, \beta)$ starting with small values of M was not used because of loss of accuracy by subtraction. Instead we used backwards recursion,

$$F(M-1, 0; \alpha, \beta)$$

$$= \frac{1}{M-1}\left(\frac{(M-2)!}{(\alpha+\beta)^{M-1}} + \alpha F(M, 0; \alpha, \beta)\right) \quad \text{(A9)}$$

and started by approximately evaluating the integral for a high value of M by an asymptotic series:

$$\int_r^{\infty} \frac{ds}{s} e^{-\beta s} = \frac{e^{-\beta r}}{\beta r} \sum_{k=0}^{n} \frac{(-1)^k k!}{(\beta r)^k}$$

$$+ \frac{(n+1)!(-1)^{n+1}}{\beta^{n+1}} \int_r^{\infty} \frac{ds}{s^{n+2}} e^{-\beta s}$$

after $n + 1$ partial integrations. This gives the asymptotic expansion

$$F(M, 0; \alpha, \beta) = \sum_{k=0}^{n} \frac{(-1)^k(M-k-2)!k!}{(\alpha+\beta)^{M-k-1}\beta^{k+1}} + r_n,$$

(A10)

where

$$|r_n| < \frac{(n+1)!}{\beta^{n+1}} \int_0^{\infty} dr\, e^{-\alpha r} r^{M-n-3} \int_r^{\infty} ds\, e^{-\beta s}$$

$$= \frac{(n+1)!}{\beta^{n+2}} \frac{(M-n-3)!}{(\alpha+\beta)^{N+N-3}} = R_n.$$

Of course, the formula (A10) is only valid as long as $n \geq M - 3$. The sum in (A10) and R_n are evaluated for several values of n; we choose as the approximate value of $F(M, 0; \alpha, \beta)$ the sum in (A10) obtained with the value of n which gives the smallest R_n. The error then diminishes for each iteration using formula (A9) as long as $M - 1 > \alpha(\alpha = 4.62, 1.34, \text{ or } 2.98)$. The scheme is checked by comparing the value obtained for $F(1, 0; \alpha, \beta)$ with

$$F(1, 0; \alpha, \beta)$$

$$= \int_0^{\infty} \frac{ds}{s} e^{-\beta s} \int_0^{s} dr\, e^{-\alpha r} = -\frac{1}{\alpha} \int_0^{\infty} \frac{ds}{s} e^{-\beta s}(e^{-\alpha s} - 1)$$

$$= \int_0^{1} dx \int_0^{\infty} ds\, e^{-(\beta+\alpha x)s} = \frac{1}{\alpha} \ln\frac{\alpha+\beta}{\beta}.$$

With our values of κ and σ[24] we obtained

$$F(50, 0; \kappa\sigma, \kappa) = 0.270\,203\,670\,5 \times 10^{23},$$

$$F(50, 0; \tfrac{1}{2}\kappa(1+\sigma), \tfrac{1}{2}k(1+\sigma)) = 0.413\,306 \times 10^{23}$$

using 16-decimal arithmetic. The error estimates R_n were too small to affect the numbers quoted. This method did not work for $F(50, 0; \kappa, \kappa\sigma)$; the asymptotic series only gave three good digits; i.e., R_n was never less than the sum in (A10) divided by 1000. This integral was computed by upwards iteration in 28-decimal arithmetic (with eight decimals a huge negative answer was obtained, showing how drastic the errors can become when an unsafe recursion formula is used). It was also computed from the formula

$$F(M, 0; \kappa, \kappa\sigma) = \frac{(M-1)!}{\kappa^M}\left(\ln\frac{1+\sigma}{\sigma} + (M-1)!\right.$$

$$\left. \times \sum_{k=1}^{M-1} \frac{(-1)^k\{1 - [\sigma/(1+\sigma)]^k\}}{k(M-k-1)!k!}\right)$$

and by truncating an infinite series

$$F(M, 0; \kappa, \kappa\sigma) = -[\gamma + \ln(\kappa\sigma)]\frac{(M-1)!}{\kappa^M} - I(M)$$

$$-\sum_{k=1} \frac{(-\kappa\sigma)^k}{k^{M+k}} \frac{(M+k-1)!}{k\,k!} \quad,$$

$$I(M) = \int_0^\infty dr\, e^{-\kappa r} r^{M-1} \ln r$$

$$= \frac{M-1}{\kappa} I(M-1) + \frac{(M-2)!}{\kappa^M} \quad,$$

and $I(1) = -(\ln\kappa + \gamma)/\kappa$. It turns out that Euler's constant γ cancels in this expansion. None of the three methods described are very good because the terms alternate in sign, but with 28-decimal arithmetic the values obtained by the three methods agreed to nine digits:

$$F(50, 0; \kappa, \kappa\sigma) = 0.880\,736\,751 \times 10^{23} \quad.$$

Actually the last and first methods (upwards recursion) agreed to 13 digits.

To calculate the matrix elements of $H_1^{(5)}$, the integrals $A(0, M, N)$ with $M = 0$ or $N = 0$ (but $M + N \geqslant 1$) and $B(0, M, N)$ with $M = 1$ or $N = 1$ are required; thus, one needs $F(M, 0; \alpha, \beta)$ and $F(0, N; \alpha, \beta)$. For both these cases the procedure described earlier breaks down. Instead we employ a numerical method devised by Schwartz[32] which is well suited to these cases where the integrand has mild singularities at both end points. First, set $u = 1/[1 + \exp(-y)]$ to transform the region of integration from $0 \leqslant u \leqslant 1$ to $-\infty \leqslant y \leqslant \infty$ and then make the additional change of variable $x = \exp(y) - \exp(-y)$. The integral

$$\int_{-\infty}^\infty dx\, F(x)$$

is then approximated by the sum

$$\delta \sum_{n=-\infty}^{+\infty} F(n\delta)$$

truncating when the terms fall below a certain accuracy. Then the spacing δ is reduced and the sum evaluated again. This method works very well, converging fast as the spacing is decreased.

APPENDIX B: MATRIX ELEMENTS OF OPERATORS

Here we present some of the algebra involved in expressing the matrix elements of the eight operators in terms of the integrals defined in Appendix A. It is most convenient to work with one spherical component of the vector $\vec{r}_1$ in (18); we take $T_1^{(1)}(\vec{r}_1) = -(x_1 + iy_1)/\sqrt{2}$ corresponding to $m_l = L = 1$. The matrix elements are all of the form

$$M_{k'k} = \left\langle \frac{1-P_{12}}{4\pi\sqrt{2}} T_1^{(1)}(\vec{r}_1) u_{l'm'n'}(1,2) \middle| H \middle| \frac{1-P_{12}}{4\pi\sqrt{2}} \right.$$

$$\left. \times T_1^{(1)}(\vec{r}_1) u_{lmn}(1,2) \right\rangle , \quad (B1)$$

where

$$u_{lmn}(1, 2) = e^{-1/2\kappa\sigma r_1} e^{-1/2\kappa r_2} r_1^m r_2^n r_{12}^l$$

and the ordering $(l', m', n') \rightarrow k'$; $(l, m, n) \rightarrow k$ is implied. H is any of the eight operators, and every one of these is symmetric in the coordinates of the two electrons, $H = H(1, 2) = H(2, 1)$, so that

$$M_{k'k} = \int \frac{dv_1}{4\pi} \int \frac{dv_2}{4\pi} [T_1^{(1)*}(\vec{r}_1) u_{l'm'n'}(1,2)$$

$$- T_1^{(1)*}(\vec{r}_2) u_{l'm'n'}(2,1)] H T_1^{(1)}(\vec{r}_1) u_{lmn}(1,2).$$

Whenever we have more than one differential operator (∇_1 or ∇_2), it is preferable to let all operators act to the the right. The matrix elements are then sums of terms whose coefficients only depend on unprimed indices, so that the actual programs are unsymmetric in the indices. The matrices of the eight operators are all symmetric, since the matrix elements are real and the operators Hermitian. If one lets one ∇ operator act to the left and one act to the right, the program will be symmetric in primed and unprimed indices and can produce a symmetric matrix even if the integrals used are wrong. When all operators act to the right, the computed matrices will be unsymmetric if the integrals have incorrect values. We thus get a check on the integrals by letting all operators act to the right; several errors in the programs were detected this way.

We now discuss the operators one by one.

The nonrelativistic Hamiltonian H_0 is given by (5):

$$H_0 T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) = \left(T_1^{(1)}(\vec{r}_1)\left\{ \tfrac{1}{8}\kappa^2(\sigma^2+1) + (1/r_1)[\tfrac{1}{4}\kappa\sigma(2m+4+l) - Z] + (1/r_2)[\tfrac{1}{4}\kappa(2n+2+l) - Z] - (1/r_1^2)\tfrac{1}{2}m(m+3+l) \right.\right.$$

$$- (1/r_2^2)\tfrac{1}{2}n(n+1+l) - (1/r_{12}^2)\tfrac{1}{2}l(2l+4+m+n) + (1/r_{12}) + (r_1/r_{12}^2)\tfrac{1}{4}\kappa\sigma l + (r_2/r_{12}^2)\tfrac{1}{4}\kappa l + (r_2^2/r_1^2 r_{12}^2)\tfrac{1}{2}ml$$

$$+ (r_1^2/r_2^2 r_{12}^2)\tfrac{1}{2}ml - (r_2^2/r_1 r_{12}^2)\tfrac{1}{4}\kappa\sigma l - (r_1^2/r_2 r_{12}^2)\tfrac{1}{4}\kappa l\right\} + T_1^{(1)}(\vec{r}_2)(l/r_{12}^2)\right) u_{lmn}(1, 2)$$

$$\equiv \left[T_1^{(1)}(\vec{r}_1)\left(\sum_{i=1}^{13} c_i(l, m, n; \kappa\sigma, \kappa) r_1^{p_i} r_2^{q_i} r_{12}^{s_i} \right) + T_1^{(1)}(\vec{r}_2) \frac{l}{r_{12}^2} \right] u_{lmn}(1, 2) . \quad (B2)$$

Introducing $L = l + l'$, $M_D = m + m'$, $N_D = n + n'$, and $N_e = n + m'$ one gets the following formula for the matrix elements:

$$(M_0)_{k'k} = \frac{1}{3} \sum_{i=1}^{13} c_i \, (l, m, n \, ; \, \kappa\sigma, \kappa) \, [\, A_{DI}(L + 2 + s_i , \, M_D + 4 + p_i , \, N_D + 2 + q_i)$$

$$- B_{EX}(L + 2 + s_i , \, M_E + 3 + p_i , \, N_E + 3 + q_i) \,] + l[B_{DI}(L, \, M_D + 4, \, N_D + 2) - A_{EX}(L, \, M_E + 3, \, N_E + 3)] \quad .$$

It is convenient to write out $H_1^{(i)} T_1^{(1)} (\vec{r}_1) u_{lmn}(1, 2)$ in detail to see what terms, other than the standard ones, are required in the expansions of $\psi_1^{(i)}$ for $H_0 \psi_1^{(i)}$ to reproduce the most singular terms in $H_1^{(i)} \psi_0$. Since we only consider intermediate triplet P states, the P parts are projected out when three spin-dependent operators act on ψ_0. The angular momenta of the unperturbed state are fixed by choosing the "stretched" state, i.e., $J = m_J = 2$ so that the spin part of the wave function is $\alpha(1) \alpha(2)$. We have

$$H_1^{(1)} \alpha(1)\alpha(2) T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) = Z \left\{ \alpha(1)\alpha(2) \left[\frac{1}{r_1^3} + l \, \frac{(\vec{r}_1 \times \vec{r}_2)_0}{i \, r_{12}^2} \left(\frac{1}{r_2^3} - \frac{1}{r_1^3} \right) \right] \right.$$

$$\left. - \frac{1}{\sqrt{2}} \, [\alpha(1)\beta(2) + \alpha(2)\beta(1)] l \, \frac{(\vec{r}_1 \times \vec{r}_2)_{+1}}{i \, r_{12}^2} \left(\frac{1}{r_2^3} - \frac{1}{r_1^3} \right) \right\} \, T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) \, , \quad \text{(B3)}$$

where vectors have been resolved in spherical components

$$(v)_{\pm} = \mp (V_x \pm i V_y)/\sqrt{2}, \quad v_0 = v_z , \quad (\vec{r}_1 \times \vec{r}_2)_\lambda = -i\sqrt{2} \, T_\lambda^{(1)}(\vec{r}_1 \times \vec{r}_2) = -i\sqrt{2} \sum_\mu C(111 \, ; \lambda \, \mu) T_\mu^{(1)}(\vec{r}_1) \, T_{\lambda-\mu}^{(1)} (\vec{r}_2) \quad (\lambda = +1, 0, -1)$$

by the usual law for combining spherical tensors; $C(l_1 l_2 l \, ; m_1 m_2)$ are Clebsch-Gordan (CG) coefficients. The second term in (B3) is pure D, the first term is a mixture of P and D. The P part of

$$- \sqrt{2} \, T_0^{(1)} (\vec{r}_1 \times \vec{r}_2) T_1^{(1)} (\vec{r}_1)$$

is

$$- (1/\sqrt{2}) \, [T_0^{(1)}(\vec{r}_1 \times \vec{r}_2) T_1^{(1)}(\vec{r}_1) - T_1^{(1)}(\vec{r}_1 \times \vec{r}_2) \, T_0^{(1)}(\vec{r}_1)] = \tfrac{1}{2} \, [T_1^{(1)} (\vec{r}_1) (\vec{r}_1 \cdot \vec{r}_2) - T_1^{(1)} (\vec{r}_2) \, r_1^2] \, ,$$

which is proportional to $[\vec{r}_1 \times (\vec{r}_1 \times \vec{r}_2)]_{+1}$. So the P part of (B3) is

$$Z \alpha(1)\alpha(2) \left[\frac{1}{r_1^3} T_1^{(1)} (\vec{r}_1) + \frac{l}{2 r_{12}^2} \left(\frac{1}{r_2^3} - \frac{1}{r_1^3} \right) [T_1^{(1)} (\vec{r}_1) (\vec{r}_1 \cdot \vec{r}_2) - T_1^{(1)} (\vec{r}_2) \, r_1^2] \right] u_{lmn}(1, 2) \, . \quad \text{(B4)}$$

The terms proportional to l only contribute exchange integrals to the matrix elements. Since

$$\vec{r}_2 \cdot [\vec{r}_1 \times (\vec{r}_1 \times \vec{r}_2)] = - r_1^2 r_2^2 \sin^2 \theta_{12} \, ,$$

we use (A4) to obtain a simple formula for the matrix elements:

$$(M_1^{(1)})_{k'k} = \tfrac{1}{3} Z \{ A_{DI} (L + 2, \, M_D + 1, \, N_D + 2) - (1/L) \, [\, l B_{EX}(L + 2, \, M_E + 3, \, N_E) + l' \, b_{EX}(L + 2, \, M_E , \, N_E + 3)] \} \quad .$$

Proceeding to the next operator we obtain, after a similar angular momentum projection, the expression

$$P \text{ part of } H_1^{(2)} \alpha(1)\alpha(2) T_1^{(1)} (\vec{r}_1) u_{lmn}(1, 2) = \alpha(1)\alpha(2) \left(\frac{-3}{r_{12}^3} \right) \left\{ T_1^{(1)}(\vec{r}_1) - T_1^{(1)}(\vec{r}_2) \right.$$

$$\left. + \frac{1}{2} \left(- \frac{\kappa\sigma}{2} \, \frac{1}{r_1} + \frac{m}{r_1^2} + \frac{\kappa}{2} \, \frac{1}{r_2} - \frac{n}{r_2^2} \right) \, [T_1^{(1)}(\vec{r}_1)(\vec{r}_1 \cdot \vec{r}_2) - T_1^{(1)} (\vec{r}_2) \, r_1^2] \right\} u_{lmn}(1, 2) \, . \quad \text{(B5)}$$

The integrals contributing to the matrix elements are easy to write down. The first two terms must be treated separately when $L = 0$, when the formula

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \, \frac{1}{r_{12}^3} = \frac{1}{r_> \, (r_>^2 - r_<^2)}$$

is used, in which case F integrals are needed. Since

$$\vec{r}_1 \cdot (\vec{r}_1 - \vec{r}_2) = \tfrac{1}{2} \, (r_1^2 - r_2^2 + r_{12}^2),$$

$$\vec{r}_2 \cdot (\vec{r}_1 - \vec{r}_2) = \tfrac{1}{2}(r_1^2 - r_2^2 - r_{12}^2) \, ,$$

the factor $(r_>^2 - r_<^2)$ cancels out. As with $H_1^{(1)}$, the remaining terms only give exchange integrals, and (A4) is used again, except when $L = 1$, when the formula

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \, \frac{\sin^2 \theta_{12}}{r_{12}^2}$$

$$= \frac{r_1^2 + r_2^2}{4 r_1^2 r_2^2} - \frac{(r_1^2 - r_2^2)^2}{8 r_1^3 r_2^3} \ln \frac{r_1 + r_2}{|r_1 - r_2|}$$

is used, so that F_L integrals are required. The

spin-spin operator is a contraction of two tensors of rank two:

$$H_1^{(3)} = -\frac{3}{r_{12}^5} \sum_{\mu=-2}^{\mu=+2} S_{-\mu}^{(2)} T_\mu^{(2)}(\vec{r}_{12})(-1)^\mu .$$

Only the spin-operator $S_\mu^{(2)}$ with $\mu = 0$ gives back the spinor $\alpha(1)\alpha(2)$ when it acts on that state; we have

$$S_0^{(2)}\alpha(1)\alpha(2) = (1/\sqrt{6})(2\sigma_{1z}\sigma_{2z} - \sigma_{1x}\sigma_{2x} - \sigma_{1y}\sigma_{2y})\alpha(1)\alpha(2)$$

$$= \sqrt{\tfrac{2}{3}}\, \alpha(1)\alpha(2).$$

$T_0^{(2)}(\vec{r}_{12})T_1^{(1)}(\vec{r}_1)$ is a combination of P, D, and F parts:

P part of $T_0^{(2)}(\vec{r}_{12})T_1^{(1)}(\vec{r}_1)$

$= P$ part of $(1/\sqrt{6})(2z_{12}^2 - x_{12}^2 - y_{12}^2)T_1^{(1)}(\vec{r}_1)$

$= (1/\sqrt{10})[\sqrt{\tfrac{3}{5}}\, T_2^{(2)}(\vec{r}_{12})\, T_{-1}^{(1)}(\vec{r}_1) - \sqrt{\tfrac{3}{10}}\, T_1^{(2)}(\vec{r}_{12})T_0^{(1)}(\vec{r}_1)$

$+ (1/\sqrt{10})\, T_0^{(2)}(\vec{r}_{12})T_1^{(1)}(\vec{r}_1)]$

$= \tfrac{1}{10}\sqrt{\tfrac{2}{3}}\, [T_1^{(1)}(r_1)r_{12}^2 - 3T_1^{(1)}(r_{12})\vec{r}_{12}\cdot\vec{r}_1]$

after some CG algebra. It was necessary to express $T_\mu^{(2)}(\vec{r}_{12})$ in terms of $T_\lambda^{(1)}(\vec{r}_1)$ and $T_\lambda^{(1)}(\vec{r}_2)$; one can use a formula due to Rose[33] or work the relations out by inspection. We quote one example:

$$T_0^{(2)}(\vec{r}_{12}) = T_0^{(2)}(\vec{r}_1) + T_0^{(2)}(\vec{r}_2) - 2\sqrt{\tfrac{2}{3}}\, T_0^{(1)}(\vec{r}_1)T_0^{(1)}(\vec{r}_2)$$

$$- \sqrt{\tfrac{2}{3}}\,[\, T_{-1}^{(1)}(\vec{r}_1)T_1^{(1)}(\vec{r}_2) + T_1^{(1)}(\vec{r}_1)T_{-1}^{(1)}(\vec{r}_2)] .$$

The result is

P part of $H_1^{(3)}\alpha(1)\alpha(2)T_1^{(1)}(\vec{r}_1)u_{lmn}(1,2)$

$= \tfrac{1}{5}(1/r_{12}^5)\alpha(1)\alpha(2)[\, 3T_1^{(1)}(\vec{r}_{12})(\vec{r}_{12}\cdot\vec{r}_1)$

$- T_1^{(1)}(r_1)r_{12}^2\,]u_{lmn}(1,2) .$ (B6)

For the matrix elements one gets

$$(M_1^{(3)})_{k'k} = \frac{1}{10}\int\frac{dv_1}{4\pi}\int\frac{dv_2}{4\pi}\left[\left(\frac{(r_1^2-r_2^2)^2}{2r_{12}^5} + \frac{r_1^2-3r_2^2}{3r_{12}^3} + \frac{1}{2r_{12}}\right)u_{l'm'n'}(1,2)\right.$$

$$\left. -\left(\frac{(r_1^2-r_2^2)^2}{2r_{12}^5} - \frac{r_1^2+r_2^2}{3r_{12}^3} - \frac{1}{6r_{12}}\right)u_{l'm'n'}(2,1)\right]u_{lmn}(1,2) ,$$

which can easily be expressed in terms of A, F, and F_L integrals, when the cases $L = l + l' = 0, 1, 2,$ and 3 are given special treatment. The formulas

$$\int\frac{d\Omega_1}{4\pi}\int\frac{d\Omega_2}{4\pi}\frac{1}{r_{12}^5} = \frac{r_<^2 + 3r_>^2}{3r_>(r_>^2 - r_<^2)^3} ,$$

$$\int\frac{d\Omega_1}{4\pi}\int\frac{d\Omega_2}{4\pi}\frac{1}{r_{12}^4} = \frac{1}{(r_1^2 - r_2^2)^2}$$

are required. For $L = 0$ all terms with $(r_1^2 - r_2^2)^{-2}$ cancel.

We have dropped the constant $\tfrac{1}{4}\alpha^2$ from the spin-dependent Breit operators in this discussion as well as in the actual calculations; the factor is included in the units in which the numerical results are given.

Proceeding now to the spin-independent operators, we shall just write out the result of the action of $H_1^{(4)}$ on one of the trial functions. After some tedious but trivial algebra we obtain, omitting α^2,

$$H_1^{(4)}T_1^{(1)}(\vec{r}_1)u_{lmn}(1,2) = \frac{1}{2}\left\{T_1^{(1)}(\vec{r}_1)\left(-\frac{3\kappa}{4}\frac{1}{r_{12}r_2} + \frac{3n}{2}\frac{1}{r_{12}r_2^2} + \frac{2l+\tfrac{1}{2}n}{r_{12}} - \frac{\kappa}{4}\frac{r_2}{r_{12}^3} + \frac{\kappa}{4}\frac{r_1^2}{r_2r_{12}^3} - \frac{n}{2}\frac{r_1^2}{r_{12}^3r_2^2}\right)\right.$$

$$+ T_1^{(1)}(\vec{r}_1)\left[-\frac{l(2l+2+m+n)+\tfrac{1}{2}n(m+1)}{r_{12}^3} + \frac{\kappa^2\sigma}{8}\left(\frac{r_1}{r_{12}r_2} + \frac{r_2}{r_{12}r_1}\right) + \frac{\kappa^2\sigma}{16}\left(\frac{r_1^3}{r_{12}^3r_2} + \frac{r_2^3}{r_{12}^3r_1} - \frac{2r_1r_2}{r_{12}^3} - \frac{3r_{12}}{r_1r_2}\right)\right.$$

$$+ \frac{\kappa\sigma}{4}(2l+n)\frac{r_1}{r_{12}^3} + \frac{\kappa}{4}(2l+1+m)\frac{r_2}{r_{12}^3} - \frac{\kappa}{4}\left(2l+1+\frac{m}{2}\right)\frac{r_1^2}{r_{12}^3r_2} - \frac{m\kappa}{8}\frac{r_2^3}{r_{12}^3r_1^2} - \frac{\kappa\sigma}{4}\left(2l+\frac{n}{2}\right)\frac{r_2^2}{r_{12}^3r_1} + 3\frac{m\kappa}{8}\frac{r_{12}}{r_1^2r_2}$$

$$+ 3\frac{n\kappa\sigma}{8}\frac{r_{12}}{r_1r_2^2} - \frac{n\kappa\sigma}{8}\frac{r_1^3}{r_{12}^3r_2^2} + \frac{n}{2}\left(2l+1+\frac{m}{2}\right)\frac{r_1^2}{r_{12}^3r_2^2} - 3\frac{mn}{4}\frac{r_{12}}{r_1^2r_2^2} + \frac{m}{2}\left(2l+\frac{n}{2}\right)\frac{r_2^2}{r_{12}^3r_1^2} + \frac{\kappa}{4}(2l+1-m)\frac{1}{r_{12}r_2}$$

$$\left.\left. - n\frac{\kappa\sigma}{4}\frac{r_1}{r_{12}r_2^2} - \frac{n}{2}(2l+1-m)\frac{1}{r_{12}r_2^2} + \frac{\kappa\sigma}{4}(2l-n)\frac{1}{r_{12}r_1} - m\frac{\kappa}{4}\frac{r_2}{r_{12}r_1^2} - \frac{m}{2}(2l-n)\frac{1}{r_{12}r_1^2}\right]\right\}u_{lmn}(1,2).$$ (B7)

The matrix elements can now be written in terms of A, B, F, and F_L integrals, again in the cases when $L = 0$, 1 all terms with r_{12}^{-3} must be taken care of specially.

If we write out directly the action of $H_1^{(5)}$ on the trial functions we get 112 terms. To evaluate its matrix elements we make use of

$$\langle f \mid \nabla^4 g \rangle = \langle \nabla^2 f \mid \nabla^2 g \rangle \, ,$$

where f and g are elements of the standard basis. (This is not necessarily true if there are negative powers of r_1, r_2, or r_{12} in f or g.) It turns out that the matrix elements are sums of 225 terms. Instead of writing a program containing these terms explicitly, we let the computer do most of the work. With the notation of (B2) one has

$$\nabla_1^2 T_1^{(1)}(\vec{r}_1) u_{lmn}(1,2) = \left(-\frac{2l}{r_{12}^2} T_1^{(1)}(\vec{r}_2) + T_1^{(1)}(\vec{r}_1) \sum_{i=1}^{7} d_i (lmn; \kappa\sigma) r_{12}^{p_i} r_1^{q_i} r_2^{r_i} \right) u_{lmn}(1,2) \, ,$$

$$\nabla_2^2 T_1^{(1)}(\vec{r}_1) u_{lmn}(1,2) = \left(T_1^{(1)}(\vec{r}_1) \sum_{j=1}^{7} h_j (lmn, \kappa) r_{12}^{s_j} r_1^{t_j} r_2^{u_j} \right) u_{lmn}(1,2) \, .$$

This gives the following expression for the matrix element, again omitting α^2:

$$(M_1^{(5)})_{k'k} = -\frac{1}{24} \Bigg(\sum_{i=1}^{7} \sum_{j=1}^{7} d_i (lmn, \kappa\sigma) d_j (l'm'n'; \kappa\sigma) A_{DI}(L+2+p_i+p_j, M_D+4+q_i+q_j, N_D+2+r_i+r_j)$$

$$+ 4ll' A_{DI}(L-2, M_D+2, N_D+4) - 2l \sum_{j=1}^{7} d_j (l'm'n'; \kappa\sigma) B_{DI}(L+p_j, M_D+3+q_j, N_D+3+r_j)$$

$$- 2l' \sum_{i=1}^{7} d_i (lmn; \kappa\sigma) B_{DI}(L+p_i, M_D+3+q_i, N_D+3+r_i)$$

$$+ \sum_{i=1}^{7} \sum_{j=1}^{7} h_i (lmn; \kappa) h_j (l'm'n'; \kappa) A_{DI}(L+2+s_i+s_j, M_D+4+t_i+t_j, N_D+2+u_i+u_j)$$

$$- \sum_{i=1}^{7} \sum_{j=1}^{7} d_i (lmn; \kappa\sigma) h_j (l'm'n'; \kappa) B_{EX} (L+2+p_i+s_j, M_E+3+q_i+u_j, N_E+3+r_i+t_j)$$

$$+ 2l \sum_{j=1}^{7} h_j (l'm'n'; \kappa) A_{EX} (L+s_j, M_E+2+u_j, N_E+4+t_j)$$

$$- \sum_{i=1}^{7} \sum_{j=1}^{7} h_i (lmn; \kappa) d_j (l'm'n'; \kappa\sigma) B_{EX}(L+2+p_j+s_i, M_E+3+r_j+t_i, N_E+3+q_j+u_i)$$

$$+ 2l' \sum_{i=1}^{7} h_i (lmn, \kappa) A_{EX} (L+s_i, M_E+4+t_i, N_E+2+u_i) \Bigg) \, .$$

All the summations are done by the computer; the coefficients d_i and h_j as well as the integers (p_i, q_i, r_i) and (s_j, t_j, u_j) are determined by a subroutine once lmn is given. The program thus becomes symmetric in primed an unprimed indices, so that the computed matrix of $H_1^{(5)}$ will be symmetric even if some of the integrals have incorrect values. However, almost all the integrals used were also required for the matrices of H_0, $H_1^{(2)}$, $H_1^{(4)}$, and $H_1^{(7)}$ which were evaluated in a nonsymmetric fashion, and thus gave a valuable check on the integrals.

It is trivial to obtain the matrix elements of the contact term operator; they are zero unless $N_D = 0$, in which case we have

$$(M_1^{(6)})_{k'k} = \frac{\alpha^2}{12} \frac{K!}{(\kappa\sigma)^{K+1}} \, , \quad K = M_D + L + 4 \, .$$

Finally, the operator $H_1^{(7)}$ is quite easy after we have done $H_1^{(4)}$. Omitting the factor m/M, we have

$$H_1^{(7)} T_1^{(1)}(\vec{r}_1) u_{lmn}(1,2) = -\Bigg[T_1^{(1)}(\vec{r}_2)\left(-\frac{\kappa}{2}\frac{1}{r_2} + \frac{n}{r_2^2} + \frac{l}{r_{12}^2} \right) + T_1^{(1)}(\vec{r}_1)\left(-\frac{l(l+m+n+2)}{r_{12}^2} + \frac{l\kappa\sigma}{2}\frac{r_1}{r_{12}^2} + \frac{l\kappa}{2}\frac{r^2}{r_{12}^2} + \frac{\kappa^2\sigma}{4}\cos\theta \right.$$

$$\left. - n\frac{\kappa\sigma}{2}\frac{\cos\theta}{r_2} - m\frac{\kappa}{2}\frac{\cos\theta}{r_1} - l\frac{\kappa\sigma}{2}\frac{r_2\cos\theta}{r_{12}^2} - l\frac{\kappa}{2}\frac{r_1\cos\theta}{r_{12}^2} + mn\frac{\cos\theta}{r_1 r_2} + ml\frac{r_2\cos\theta}{r_1 r_{12}^2} + nl\frac{r_1\cos\theta}{r_2 r_{12}^2} \right) \Bigg] u_{lmn}(1,2) \, .$$

(B8)

To evaluate the exchange part of the matrix elements we use $\cos^2\theta = 1 - \sin^2\theta$ and (A4), or we may rewrite (B8) using

$$\cos\theta = \frac{r_1^2 + r_2^2 - r_{12}^2}{2 r_1 r_2} \; .$$

Only A and B integrals are required to calculate the matrix elements of $H_1^{(7)}$.

This concludes the description of the evaluation of matrix elements of the operators. The formulas of this appendix will be used also in later papers, where we go beyond the standard basis and include one negative power of r_1, r_2, or r_{12} in the expansions for $\psi_1^{(i)}$.

APPENDIX C: SPIN-INDEPENDENT SECOND-ORDER ENERGIES

The spin-independent second-order energies calculated along with the spin-dependent ones in Sec. VI are listed in Table VI, with the same convention for the number of digits quoted as in Sec. VI.

The unmixed second-order energies $E_2^{(i,i)}$ ($i = 1$, $2, \ldots, 7$) that we calculate are always upper bounds to the true values. The exact unmixed second-order energy is given by (14):

$$E_2^{\text{true}} = \langle \Psi_1 \mid H_0 - E_0 \mid \Psi_1 \rangle + 2 \langle \Psi_1 \mid H_1 - E_1 \mid \Psi_0 \rangle \; ,$$
(C1)

where the (exact) perturbed function Ψ_1 satisfies

$$(H_0 - E_0)\Psi_1 = -(H_1 - E_1)\Psi_0 \; ,$$
(C2)

assuming that the unperturbed wave function and energy Ψ_0 and E_0 are known exactly. In practice the expression (C1) is calculated by using an approximation ψ_1 to Ψ_1, $\psi_1 = \Psi_1 + \Delta \psi_1$, so that

$$E_2^{\text{calc}} = E_2^{\text{true}} + \langle \Delta\psi_1 \mid H_0 - E_0 \mid \Delta\psi_1 \rangle$$

$$+ 2 \langle \Delta\psi_1 \mid H_0 - E_0 \mid \Psi_1 \rangle + 2 \langle \Delta\psi_1 \mid H_1 - E_1 \mid \Psi_0 \rangle \; .$$
(C3)

The two last terms of (C3) cancel because of (C2); the second term of (C3) is seen to be positive if $\Delta\psi_1$ is expanded in the complete set of (triplet P) eigenfunctions of H_0, remembering that E_0 is the lowest (triplet P) eigenvalue. Thus we have $E_2^{\text{calc}} \geq E_2^{\text{true}}$, as we set out to prove, but this does not necessarily imply that E_2 should decrease monotonically as more terms are included in the expansion for ψ_1. However, in all the calculations reported here, this monotonic decrease does in fact take place.

Notice that the differences between successive calculations for $E_2^{(5,5)}$, $E_2^{(5,6)}$, and $E_2^{(6,6)}$ are almost constant, so that extrapolation of these values would give infinite results. This is just as it should be since both $H_1^{(5)}$ and $H_1^{(6)}$ give δ functions when acting on ψ_0; thus $\psi_1^{(5)}$ and $\psi_1^{(6)}$ should have terms propor-

TABLE VI. Second-order spin-independent perturbation energies, using only standard terms (18) in the expansions for $\psi_1^{(i)}$ ($i = 4$, 5, 6, 7).

	$E_2^{(4,4)}[2\alpha^4 R]$	$E_2^{(5,5)}[2\alpha^4 R]$	$E_2^{(6,6)}[2\alpha^4 R]$	$E_2^{(7,7)}[2(m/M)^2 R]$	$E_2^{(4,5)}[2\alpha^4 R]$	$E_2^{(4,6)}[2\alpha^4 R]$	$E_2^{(4,7)}[2\alpha^2(m/M)R]$	$E_2^{(5,6)}[2\alpha^4 R]$	$E_2^{(5,7)}[2\alpha^2(m/M)R]$	$E_2^{(6,7)}[2\alpha^2(m/M)R]$
1	−0.019 941 220 293	−252.299 578 45	−89.151 341 771	−0.067 054 443 539	−0.509 607 895 26	0.297 444 545 40	0.033 581 361 648	149.929 604 28	1.179 844 500 8	−0.668 956 889 07
2	−0.028 765 953 478	−349.322 543 8	−108.818 603 13	−0.121 394 680 80	−0.038 045 570 52	0.017 125 440 41	0.053 384 471 490	194.065 283 44	−0.128 063 566 6	−0.020 398 608 31
3	−0.033 335 806 32	−442.929 537 3	−133.136 851 57	−0.142 266 384 00	−0.103 235 054 58	0.092 956 846 87	0.062 084 852 257	241.747 062 34	0.454 101 286 99	−0.320 344 711 7
4	−0.035 906 828 84	−534.409 237 7	−155.751 708 49	−0.160 864 025 2	−0.040 438 852 6	0.064 126 857	0.067 951 065 59	287.235 104 7	0.068 818 01	−0.134 151 816
5	−0.037 393 840	−621.797 41	−177.726 7	−0.180 662 90	−0.073 332 5	0.082 165 0	0.072 383 33	331.051 16	0.367 001 8	−0.287 356 4
6	−0.038 073 6	−708.1	−199.26	−0.191 578	−0.055 52(1)	0.074 06	0.074 448 9	371.4	0.167 1	−0.189 4
7	−0.038 343 7	−793.0	−220.50	−0.196 15	−0.062 56(1)	0.077 96(1)	0.075 196	416.6	0.287 6(1)	−0.249 9
8	−0.038 447 9	−877.3	−241.56	−0.200 10	−0.055 9(2)	0.074 91(1)	0.075 703	458.7	0.199 2(1)	−0.206 1

tional to $(1 - P_{12})T_1^{(1)}(\vec{r}_1)/r_2$. This makes the second-order energies $E_2^{(i,j)} = \langle \psi_1^{(i)} | H_1^{(j)} - E_1^{(j)} | \psi_0 \rangle$ ($i, j = 5, 6$) proportional to an integral with $\delta^{(3)}(\vec{r}_2)$ (from $H_1^{(j)}$) and $1/r_2$ (from $\psi_1^{(i)}$) and ψ_0 under the integral sign, and this is obviously divergent.

Otherwise, the energies $E_2^{(4,5)}$, $E_2^{(4,6)}$, $E_2^{(5,7)}$, and $E_2^{(6,7)}$ show fairly regular oscillatory behavior with ω, i.e., differences between successive calculations alternate in sign, and $E_2^{(4,4)}$, $E_2^{(7,7)}$, and $E_2^{(6,7)}$ seem to converge monotonically.

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