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SECOND-ORDER CORRECTIONS TO THE FINE-STRUCTURE OF HELIUM

Lars Hambro
(Ph. D. Thesis)

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SECOND-ORDER CORRECTIONS TO THE FINE-STRUCTURE OF HELIUM

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ABSTRACT

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 wavefunction by the variational method. The second-order contributions are then given by a single integral. These corrections are first calculated using standard Hylleraas-expansions with up to 165 terms for the perturbed wavefunctions, 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. These variational calculations are improved by including additional terms, reflecting the singularities of the Breit operators, in the expansions. With this refinement another five contributions are obtained to the accuracy of 10^{-6} cm^{-1} required by the larger fine-structure interval. It will require much more effort to match the experimental precision of 10^{-7} cm^{-1} in the smaller interval, but we have shown that the second-order perturbations of the larger interval can be calculated accurately enough to permit a new high-precision determination of the fine-structure constant.

I. INTRODUCTION

Today there are several accurate values of the Sommerfeld fine structure constant $\alpha = e^2/\hbar c \approx 1/137$ 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 1965 tabulation of the fundamental constants. This has come to be regarded as the "official" value of α, but it is now very much in doubt. From recent measurements of the $2S_{1/2}$ - $2P_{3/2}$ fine structure in hydrogen, Kaufman et al.[4] obtain $\alpha^{-1} = 137.0350(4)$ and Metcalf et al.[5] get $\alpha^{-1} = 137.0353(8)$ from level crossing experiments in hydrogen.

The ac Josephson effect provides a method for measuring 2e/h directly, from which α can be obtained without use of QED. From their most recent determination of 2e/h,[6] Parker, Langenberg and Taylor obtain[7] $\alpha^{-1} = 137.03608(26)$, so the accuracy is 1.9 parts per million (1.9 ppm).

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 line-width for the 2^3P state of helium is thus about 3 Mc/sec, whereas for the 2^2P state of deuterium (or hydrogen) it is about 100 Mc/sec. So one should be able to 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 (see Fig. 1), and α can in principle be determined from either one. The smaller interval has been measured to[8] $\nu_{12} = 2291.195(7)$ Mc/sec or to 3 ppm. The present best value of the larger interval is $\nu_{01} = 29616.88(7)$ Mc/sec,[9] good to 2.3 ppm. Kaufman et al.[4] determine the $2S_{1/2} - 2P_{3/2}$ splitting in hydrogen to 3 ppm, but to obtain the fine structure they must subtract the experimental value of the Lamb shift; the resulting accuracy of the fine structure is only 6 ppm. So the helium measurements are more accurate than the ones for hydrogen; and it should be possible to improve the experimental value for ν_{01} to 1 ppm.[10]

Since the fine-structure intervals are proportional to the square of α (to lowest order in α), one can in principle obtain α to 1.5 ppm from the helium measurements that have already been done, and maybe eventually get α to 0.5 ppm from the experimental value of ν_{01}.

However, there is at present no theoretical formula for the fine structure of helium with terms up to, and including, the order $\alpha^6 mc^2$, say, such as there is 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,[11,12] this project consists of several fairly distinct jobs.

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

$$E_J - E_0 = \alpha^2 \langle 0|H_2|0\rangle_J + \alpha^4 \langle 0|H_2 \frac{1}{E_0 - H_0} H_2|0\rangle_J + \alpha^4 \langle 0|H_4|0\rangle_J + (\text{terms of order } \alpha^5 \text{ and higher}) . \qquad (1)$$

Here H_0, E_0 and $|0\rangle$ are the nonrelativistic Hamiltonian, the energy of the (unperturbed) 2^3P state in atomic energy units, 2 Ry = $mc^2\alpha^2$, and

the corresponding nonrelativistic wavefunction, respectively:

$$H_0|0\rangle = E_0|0\rangle \quad .$$

The subscript J denotes spin dependence, $\vec{J} = \vec{L} + \vec{S}$ 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,[13-16] 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 the leading term on the right hand side of (1) to 1 ppm. This task has been accomplished by Schwartz[11] who evaluated the expectation values of the spin-dependent Breit operators for a sequence of variational wavefunctions $|0\rangle$, using a Hylleraas-like expansion with half powers for $|0\rangle$, with up to 439 terms in the expansion. Second, the calculation of the second-order perturbation energies

$$\langle 0|H_2^{(1)} \frac{1}{E_0 - H_0} H_2^{(2)}|0\rangle \qquad (2)$$

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 job which we shall try to do in this work. Third, 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 quantum electrodynamic know-how since it is at the same level (same powers of α) as the most recent[2] QED work on hydrogen. However, a simplifying feature is that only spin-dependent operators are required. A first attempt at this analysis was made by Kim.[16] He started with a Dirac-type Hamiltonian and added a quantized, transverse electromagnetic field to the instantaneous Coulomb interaction between the two electrons. Expanding everything in powers of α and reducing to a Pauli-type Hamiltonian he obtained H_0, all the Breit terms and a large number of complicated operators proportional to α^4. This is not quite correct, since it does not provide for creation and annihilation of electrons and positrons. A more complete analysis, starting from the Bethe-Salpeter equation is in progress.[17] Finally, the fourth job is to evaluate the expectation value of H_4 to 1%. Work is in progress on this calculation,[18] using the operators that Kim obtained; since they are quite complicated, this is not a trivial task.

In addition to the terms in (1) there are other corrections due to the anomalous magnetic moment of the electron (which gives a α^3 term in (1)), which is quite simple; then the reduced mass must be put in and there is also the operator $\vec{p}_1 \cdot \vec{p}_2/M$ correcting for the motion of the nucleus which will contribute 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 well known results[20] from hydrogen. Schwartz[11] has given an argument to show that a finite charge distribution of the nucleus (smeared over nuclear distances $R \sim 10^{-13}$ cm) has negligible effect. The leading term in the fine structure is proportional to

$\langle\xi(r)\rangle = \langle(1/r)\ \partial V/\partial r\rangle \sim \langle 1/r^3\rangle$; a deviation from a pure Coulomb potential V for distances $r < R$ adds to the fine structure of an ℓ-electron an amount

$$\frac{\int_0^R r^2 dr[\xi'(r) - \xi(r)]r^{2\ell}}{\int_0^{a_0} r^2 dr\xi(r)r^{2\ell}}$$

times the fine structure, where a_0 is the Bohr radius ($\sim 10^{-8}$ cm) and $\xi'(r)$ is derived from the "true" potential for $r < R$. Assuming that we get an upper limit by putting $\xi' = 0$, the above factor is of the order $(R/a_0)^{2\ell} \leq (R/a_0)^2 \sim 10^{-10}$, and thus completely negligible. The same argument can be used to show that vacuum polarization modifications to the nuclear potential also are insignificant; vacuum polarization smears the charge distribution to distances of order of the electron Compton wavelength which is α times smaller than the Bohr radius; then we have an additional factor α from the Feynman diagram for vacuum polarization, so that the effect of vacuum polarization is $\alpha(\alpha^2)$ times the fine structure; again negligible. (This would give a α^5 term in (1).)

The second order energy (2) is usually evaluated, formally at least, by inserting a complete set of states:

$$\sum_n{}' \frac{\langle 0|H_2^{(1)}|n\rangle\langle n|H_2^{(2)}|0\rangle}{E_0 - E_n} \tag{3}$$

but this method is certainly not practical for the present problem since we do not have a complete set of helium wavefunctions at our disposal. Instead we shall start out by solving an inhomogeneous Schrödinger equation for the perturbation to the wavefunction. This can be formulated as a variational principle, so that we get a problem similar to the original Hylleraas-problem of finding the ground state nonrelativistic helium wavefunction, except that in the present case there is no unknown energy

eigenvalue in the variational principle. Once the perturbation to the wavefunction has been found, the second order perturbation energy (2) is given by a single integral.

We point out that there are several very sound reasons for a determination of α to 1 ppm. For one thing, as a matter of pride, one would like to know α to the same precision as, say, the velocity of light and the Rydberg for infinite mass (c is known to 0.33 ppm and R_∞ to 0.10 ppm[7]). But more important is the fact that a high-accuracy value of α is needed to compare the predictions of QED with precision experiments; the most important of these are on the anomalous magnetic moments of electrons and muons, and the hyperfinestructures (hfs) of hydrogen and muonium. Parker et al.[7] insert their non-QED value of α in the most recent theoretical expressions and compares with the latest experiments. The theoretical value of $a_e = (g_e - 2)/2$ for the electron is known to 2 ppm, where the dominant contribution to the uncertainty comes from α. Clearly, if one is to see the small α^3 corrections to a_e (a current estimate of this term is $0.13\ (\alpha/\pi)^3$) one would have to know α to 1 ppm or better. The experimental value of a_e is good to 23 ppm, but it does not agree well with the theoretical one:

$$a_e(\text{experimental}) - a_e(\text{theory}) = (-\ 81\pm30) \times 10^{-9} \quad \text{(Ref. 7)}$$

This seems to indicate disagreement between experiment and theory; but the experimental result involves some tricky corrections,[7] and should perhaps be taken with a grain of salt. For muons, a_μ has been measured to 270 ppm, and the theory is good to 135 ppm[7]; the uncertainty in α is not important here. Agreement with theory is again poor:

$$a_\mu(\text{experimental}) - a_e(\text{theory}) = (+\ 55\pm^{31}_{35}) \times 10^{-8} \quad \text{(Ref. 7)}$$

and the discrepancy has the opposite sign of that of the electron. If a_μ can be determined to higher accuracy, one might hope to see hadronic contributions to a_μ from such things as vacuum polarization by pion pairs. Before that can be done, one must know the α^3 corrections to a_μ; work on this seems to be in progress.[21] This gives a compelling motivation to find α to 1 ppm. The hydrogen hfs has been measured to an incredible relative accuracy of 1.2×10^{-13} (Ref. 22) (the most precise measurement of any physical quantity, published in a hard-to-find engineering journal). Theory is far from definitive because the hadronic corrections due to the proton are somewhat speculative; using present estimates of nuclear recoil, but omitting a proton polarizability contribution δ, one gets a result for the hfs accurate to 4 ppm, where most of the uncertainty comes from α. This agrees well with experiment:

$$\frac{\text{hfs(experiment)} - \text{hfs(theory)}}{\text{hfs(experiment)}} = (2.5 \pm 4.0)\ \text{ppm} - \delta \qquad \text{(Ref. 7)}$$

Clearly, a better value of α is required if one wants to obtain information on δ from the accurate hydrogen hfs experiments. Muonium hfs has been measured to 9 ppm, but the theory is only good to 14 ppm due to the uncertainty in the theoretical value of the diamagnetic shielding correction to muons in water. Within the uncertainties, the agreement between theory and experiment is good.

Thus, although the labor involved in obtaining α to 1 ppm from helium fine structure measurements is substantial, it seems eminently worthwhile, especially since two determinations of α can be obtained. However, this assumes that QED in its present form is correct. But there is some disturbing evidence that this may not be the case; we have already mentioned the discrepancies between theory and experiment as regards the electron and muon values of $g - 2$, furthermore current measurements of hydrogenic

Lamb shifts do not agree very well with the most up-to-date theoretical values,[7] a fact which a change in the sixth digit of α^{-1} will not alter. But it would probably be rash to say that we are faced with a violation of QED at this time. One has to wait and see, in the meanwhile we proceed with our calculations of helium fine structure.

II. METHOD

The Schrödinger equation is

$$(H_0 + \lambda H_1)\Psi = E\Psi \tag{4}$$

where H_0 is the nonrelativistic Hamiltonian for helium in atomic units where the unit of length is $a_o = \hbar^2/me^2$ and the unit of energy is $e^2/a_o = \alpha^2 mc^2 = 2$ Ry:

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{5}$$

where $Z = 2$. H_1 are the Breit operators. Expanding the energy E and wavefunction Ψ in power of the "parameter of smallness" λ (in this case $\lambda = \alpha^2$):

$$\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \ldots$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots$$

inserting in (4) and equating coefficients of powers of λ we obtain:

$$H_0\Psi_0 = E_0\Psi_0 \tag{6}$$

$$H_0\Psi_1 + H_1\Psi_0 = E_1\Psi_0 + E_0\Psi_1 \tag{7}$$

$$H_0\Psi_2 + H_1\Psi_1 = E_2\Psi_0 + E_1\Psi_1 + E_0\Psi_2 \tag{8}$$

Multiply (6) by Ψ_1 and (7) by Ψ_0, integrating over all space of both particles and subtracting we get the usual result:

$$E_1 = \langle\Psi_0|H_1|\Psi_0\rangle/\langle\Psi_0|\Psi_0\rangle \tag{9}$$

assuming that H_1 is Hermitian. Once Ψ_0, E_0 and E_1 are known (7) is an inhomogeneous differential equation for the perturbation to the wavefunction Ψ_1:

$$(H_0 - E_0)\Psi_1 = -(H_1 - E_1)\Psi_0 \quad .$$

When this equation has been solved, E_2 is found by multiplying (6) by Ψ_2, (8) by Ψ_0, integrating and subtracting:

$$E_2 = \langle\Psi_0|H_1 - E_1|\Psi_1\rangle/\langle\Psi_0|\Psi_0\rangle \tag{10}$$

The perturbation H_1 is a sum of operators:

$$H_1 = \Sigma_i H_1^{(i)}$$

and so we have unmixed ($i = j$) and mixed ($i \neq j$) second-order energies:

$$E_2^{(i,j)} = \langle\Psi_0|H_1^{(i)} - E_1^{(i)}|\Psi_1^{(j)}\rangle/\langle\Psi_0|\Psi_0\rangle \tag{11}$$

The mixed energies must be counted twice in the final answers. In Eq. (11):

$$E_1^{(i)} = \langle\Psi_0|H_1^{(i)}|\Psi_0\rangle/\langle\Psi_0|\Psi_0\rangle \tag{12}$$

and

$$(H_0 - E_0)\Psi_1^{(j)} = -(H_1^{(j)} - E_1^{(j)})\Psi_0 \tag{13}$$

(11), (12) and (13) are the fundamental equations for obtaining the second-order energies $E_2^{(i,j)}$, assuming that E_0 and Ψ_0 are known. The homogeneous equation corresponding to (13) is just (6) whose solution is Ψ_0 (the solution that satisfies boundary conditions appropriate for atomic wavefunctions for some bound state), so the addition of a multiple of Ψ_0 to Ψ_1 is seen to leave the final answer $E_2^{(i,j)}$ unchanged because of (12).

We solve the inhomogeneous Schrödinger equation (13) approximately by the variational method. Consider the functional

$$E_2[\Psi_1^{(i)},\Psi_1^{(j)}] = \langle\Psi_1^{(i)}|H_0 - E_0|\Psi_1^{(j)}\rangle + \langle\Psi_1^{(i)}|H_1^{(j)} - E_1^{(j)}|\Psi_0\rangle$$
$$+ \langle\Psi_0|H_1^{(i)} - E_1^{(i)}|\Psi_1^{(j)}\rangle \tag{14}$$

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 equation (13) for $\Psi_1^{(j)}$ and the value of the functional (14) is then just the second order energy $E_2^{(i,j)}$ (11), apart from normalization. Variation with respect to $\Psi_1^{(j)}$ gives the adjoint of equation (13) 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.)

$$E_2^{(i,j)} \times \langle\Psi_0|\Psi_0\rangle = - \langle\Psi_1^{(i)}|H_0 - E_0|\Psi_1^{(j)}\rangle = - \langle\Psi_1^{(j)}|H_0 - E_0|\Psi_1^{(i)}\rangle$$
$$= \langle\Psi_0|H_1^{(i)} - E_1^{(i)}|\Psi_1^{(j)}\rangle = \langle\Psi_1^{(i)}|H_1^{(j)} - E_1^{(j)}|\Psi_0\rangle \quad (15)$$

Comparison of the numerical results obtained the four different ways will indicate the seriousness of round-off errors in our computer calculations of the second order energies.

The method of solutions 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:

$$\Psi_1^{(i)} \approx \psi_1^{(i)} = \sum_{n=1}^{N} x_n^{(i)} U_n$$

which turns (13) into a system of N inhomogeneous linear equations for $x_1^{(i)} \ldots x_N^{(i)}$:

$$\sum_{k=1}^{N} [\langle U_\ell|H_0|U_k\rangle - E_0\langle U_\ell|U_k\rangle] x_k^{(i)} = b_\ell^{(i)} \quad (16)$$
$$\ell = 1, 2, \ldots N$$

where

$$b_\ell^{(i)} = - \langle U_\ell|H_1^{(i)}|\Psi_0\rangle + E_1^{(i)}\langle U_\ell|\Psi_0\rangle \quad . \quad (17)$$

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 bad) they converge as the number N of trial functions increases.

Our choice of these trial functions will be guided by the ones used for the variational solution Ψ_0 of the homogeneous Schrödinger equation (6); which is actually more difficult to solve numerically than (13), since both the energy eigenvalue E_0 and the coefficients in the expansion of Ψ_0 are unknown, and iterative methods have to be used. We will first calculate the second order energies using the same trial functions that we use for the variational solution of (6), these functions are called the standard basis. Since Ψ_0 is an atomic wavefunction, we include a factor in the trial functions so that they fall off exponentially as $r_1 \to \infty$, $r_2 \to \infty$. This fixes the boundary condition of Ψ_0 and the $\Psi_1^{(i)}$'s at infinity. However, due to 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 ... 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, we shall eventually have 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_o 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 $H_1^{(i)}\psi_o$ has.

This approach to second order perturbation theory,[23] sometimes called the method of Dalgarno and Lewis,[24] 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[25]

in a series of papers, culminating with a very accurate calculation of the nonrelativistic Lamb shift in hydrogen (Bethe sum), and it has also been used by Schwartz[26] 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. THE NONRELATIVISTIC WAVEFUNCTION

To start the second order calculation we need the nonrelativistic wavefunction Ψ_0 which is the solution of (6). It is antisymmetric in space since we have a triplet state. Since there is no exact solution of (6), we use the time-honored variational method. The antisymmetric functions which define our standard basis are (Hylleraas basis):

$$U_{\ell mn} = \frac{1 - P_{12}}{4\pi\sqrt{2}} \vec{r}_1 \, r_1^m \, r_2^n \, r_{12}^\ell \, e^{-\frac{\kappa\sigma}{2} r_1} \, e^{-\frac{\kappa}{2} r_2} \tag{18}$$

where $\ell \geqq 0$, $m \geqq 0$, $n \geqq 0$. The variational wavefunctions are:

$$\Psi_o = \sum_{\ell,m,n=0}^{\ell+m+n\leqq\omega} C_{\ell mn} \, U_{\ell mn} \tag{19}$$

where the coefficients $C_{\ell mn}$ are determined from the variational principle. In (18) 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 wavefunctions were used by Schwartz[11] to calculate the expectation values of the spin-dependent Breit operators; with $\omega = 10$ and 286 terms in the expansion (19) 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 (19) by the replacement $C_{\ell mn} \rightarrow C_{\ell mn} + D_{\ell mn}\sqrt{r_1 + r_2}$, the goal of calculating the leading term of the fine-structure to 1 ppm was achieved with a 439-term wavefunction, but the computations had to be done in 52 decimal arithmetic. The wavefunctions (19) have been used by the author[27] to calculate the three reduced matrix elements determining the hyperfinestructure of the 2^3P level in helium 3 (which has nuclear

spin 1/2); with 165 terms the accuracy was about 1/2%.

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

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2| = (r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_{12})^{1/2}$$

where θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_2$. Other choices of variables have been made, such as "elliptic coordinates" (Ref. 13, p. 146) or the perimetric coordinates of Pekeris.[28] However, there is no particular difficulty in evaluating the many integrals with our choice of variables; fix $\vec{r}_1$, say, along the z-axis so that $\theta_{12} = \theta_2$, the azimuth of $\vec{r}_2$. The only angular integration is then over θ_2.

The expansion (19) is not the most general trial function with triplet-P symmetry, any sum of properly antisymmetrized products of two one-particle wavefunctions with arbitrarily high angular momenta ℓ_1 and ℓ_2 combined to give total angular momentum $L = 1$ is acceptable. However, most of these terms are implicit in the r_{12}-dependence in (18); Schwartz[26] has shown how the selection rules for $\vec{r}_1, \vec{r}_2$ and $\vec{r}_1 \cdot \vec{r}_2 = \frac{1}{2}(r_1^2 + r_2^2 - r_{12}^2)$ reduce the number of angular functions required, for each M_L, to $2L + 1$. In the case of $L = 1$ we have the triplet functions

$$(1 - P_{12})\, \vec{r}_1\, F(r_1, r_2, r_{12}) \qquad [(\ell_1, \ell_2) = (0,1),(1,0)]$$

With odd parity, and the even-parity function:

$$(\vec{r}_1 \times \vec{r}_2)(1 + P_{12})F(r_1, r_2, r_{12}) \qquad [(\ell_1, \ell_2) = (1,1)]$$

Since the lowest triplet-P state is sought, 2^3P, the odd-parity function is the appropriate choice since it has the symmetry of a (sp)-configuration, whereas the even function has (pp) symmetry. A (pp) configuration corresponds to a doubly excited state and has much higher energy than a singly

excited (sp) state; in fact doubly excited states lie in the continuum (Ref. 13, p. 125).

Wavefunctions 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 $0 \leqq \ell + m + n \leqq \omega$ when $\ell \geqq 0$, $m \geqq 0$ and $n \geqq \omega$ is

$$N(\omega) = \frac{1}{6}(\omega + 1)(\omega + 2)(\omega + 3) \quad . \tag{20}$$

The variational principle equivalent to the Schrödinger equation (6) is

$$\delta\langle\Psi_0|H_0 - E_0|\Psi_0\rangle = 0 \quad . \tag{21}$$

Approximating the lowest triplet-P wavefunction Ψ_0 by an expansion ψ_o of the form (19), the variational principle (18) gives

$$\delta[\sum_{k=1}^{N(\omega)} \sum_{j=1}^{N(\omega)} C_k C_j(\langle U_k|H_0|U_\ell\rangle - E_0\langle U_k|U_\ell\rangle)] = 0 \tag{22}$$

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

$$\sum_{k=1}^{N(\omega)} [(H_0)_{\ell k} - E_0 I_{\ell k}]C_k = 0 \qquad \ell = 1,2,\ldots N(\omega) \quad . \tag{23}$$

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 wavefunction $\psi_o \approx \Psi_0$ is then given by (19). The eigenvalue problem was solved by an approximate iterative method, described in Appendix C.

Ideally, the screening parameters $\kappa\sigma$ and κ should also be varied. However, differentiating the expression in square brackets in (19) 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 $(H_0)_{k\ell}$ and $I_{k\ell}$ must be calculated, which requires the computation of a lot of integrals; then the secular equation (23) 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'[11] values of κ and σ for all values of ω:

$$\kappa = 4.62 \qquad \text{and} \qquad \sigma = 0.29 \qquad \text{(Ref. 29)}$$

These two numbers are the only input for the calculations reported here. Schiff et al.[30] calculate wavefunctions and expectation values of the Breit operators for several states in helium, varying their screening parameters. However, with a 560 term wavefunction (with only integer powers of their variables) and varying the screening parameters they do not match the accuracy of Schwartz' calculation of the fine structure intervals that he obtained with 439 terms, using 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. A 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 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

$$E_1^{(1)} = 2E_0, \quad E_1^{(2)} = -E_0, \quad E_2^{(1,1)} = E_2^{(2,2)} = E_0,$$
$$E_2^{(1,2)} = E_2^{(2,1)} = -E_0 \qquad (24)$$

These relations can be deducted from the virial theorem, but it is easier to derive them from a simple scaling argument. In cgs units the Hamiltonian is

$$(H_0)_{cgs} = \frac{\hbar^2}{m}(T)_{au} + e^2(V)_{au} \qquad (25)$$

where $(T)_{au}$ and $(V)_{au}$ 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 $e^2/a_o = me^4/\hbar^2$ it follows from (25) that the scaling factor is $(1 + \mu)^2/(1 + \lambda)$. Thus the perturbed Hamiltonian H has a perturbed energy level

$$E = E_0 \frac{(1 + \mu)^2}{1 + \lambda} \approx E_0(1 + 2\mu - \lambda + \mu^2 + \lambda^2 - 2\mu\lambda) \qquad (26)$$

The relations (24) follow immediately from (26).

Because H_0 is just the sum of the two perturbations, H_0U_n will reproduce the singularities of $H_1^{(i)}\Psi_0 \approx H_1^{(i)}\psi_o$ $(i = 1,2)$, so the standard basis (18) 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 $(H_0)_{k\ell}$ 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:

$$\sum_{k=1}^{N(\omega)} A_{\ell k} X_k^{(i)} = b_\ell^{(i)} \qquad \ell = 1,2,\ldots,N(\omega) \tag{27}$$

where $A_{\ell k} = (H_0)_{\ell k} - E_0(\omega')I_{\ell k}$. Here $E_0(\omega')$ is the approximation to E_0 obtained when $N(\omega')$ terms are used in the expansion (19) for ψ_o; using this variational wavefunction in (17), the right hand side of (27) becomes

$$b_\ell^{(i)} = -\sum_{n=1}^{N(\omega')} C_n[(H_1^{(i)})_{\ell n} - E_1^{(i)} I_{\ell n}] \tag{28}$$

where

$$E_1^{(i)} = \left[\sum_{m=1}^{N(\omega')} \sum_{n=1}^{N(\omega')} C_n C_m (H_1^{(i)})_{nm}\right] \Big/ \langle\psi_o|\psi_o\rangle \tag{29}$$

and

$$\langle\psi_o|\psi_o\rangle = \sum_{m=1}^{N(\omega')} \sum_{n=1}^{N(\omega')} C_n C_m I_{nm} \tag{30}$$

The second order energies $E_2^{(i,j)}$ in (15) are given by:

$$E_2^{(i,j)} \times \langle\psi_o|\psi_o\rangle = -\sum_{m=1}^{N(\omega')} X_m^{(i)} \left(\sum_{n=1}^{N(\omega')} X_n^{(j)} [(H_0)_{nm} - E_0(\omega')I_{nm}]\right)$$

$$= -\sum_{n=1}^{N(\omega)} b_n^{(i)} X_n^{(j)} \tag{31}$$

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

If $\omega = \omega'$, then $E_0(\omega')$ has just the value which makes the matrix $A_{\ell k}$ singular, see Eq. (23). 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. We thus use the same number of standard terms in the expansions for $\psi_1^{(i)}$ and ψ_o. The singular matrix $A_{k\ell}$ then has rank $N(\omega) - 1$, because $E_0(\omega)$ is a nondegenerate eigenvalue, and we delete one equation from the system (27). One of the unknowns may be put equal to anything, and the deleted system of equations is solved fro 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 (27) are not over-determined. The coefficients C_k in the expansion (19) of ψ_o demonstrate the linear dependence among the rows of $A_{k\ell}$:

$$\sum_{k=1}^{N(\omega)} A_{\ell k}\, C_k = \langle U_\ell | H_0 - E_0(\omega) | \sum_{k=1}^{N(\omega)} C_k U_k \rangle = \langle U_\ell | H_0 - E_0 | \psi_o \rangle$$

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

The same relation holds for the right hand sides:

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

$$= \langle \psi_o | H_1^{(i)} | \psi_o \rangle - E_1^{(i)} \langle \psi_o | \psi_o \rangle = 0$$

because of (12).

Theoretically, any one of the equations in (27) may be deleted. But the most important term in the expansion (19) for ψ_o is the first one, with $\ell = m = n = 0$, corresponding to the leading (1s2p) 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 $A_{k\ell}$ is less close to being singular (has a determinant of greater magnitude) than the one obtained by deleting the nth column and row of $A_{k\ell}$ with $n > 1$. At higher dimensions $N(\omega)$ this may be important.

In Table I and Table II we present the results of the calculations in atomic units. All the computations reported in this work were done on a CDC 6600 computer in single precision arithmetic, this is 48 binary bits corresponding to slightly more than 14 decimals. When $X_2^{(i)}, X_3^{(i)} \ldots X_{N(\omega)}^{(i)}$ and $X_1^{(i)} = 0$ were inserted into the left hand side of the first equation of (27) 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_o was stopped when the difference between the eigenvalues calculated for two successive iterations were less than a certain prescribed ϵ in magnitude. For $1 \leq \omega \leq 5$ 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 wavefunction; the computations of Table I were done for these two sets of wavefunctions. The results agreed to the digits quoted. The second order energies $E_2^{(i,j)}$ were calculated by the two methods of Eq. (31) for both wavefunctions. The results using the two different methods (four in the case of $E_2^{(1,2)}$) calculated with the same wavefunction were in slightly better agreement (one more digit for $\omega = 6$, 7 and 8) than the results calculated by the same method using different wavefunctions, for both methods.

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	$\frac{1}{2}E_1^{(1)} = \frac{1}{2}\langle V\rangle$	$E_1^{(2)} = \langle T\rangle$
1	4	-2.1294717879	-2.1557992765	2.1821267650
2	10	-2.1326784020	-2.1349720423	2.1372656826
3	20	-2.1330850392	-2.1330337967	2.1329825540
4	35	-2.1331402223	-2.1331028335	2.1330654447
5	56	-2.1331575951	-2.1331389305	2.1331202659
6	84	-2.133162289	-2.13315571	2.13314913
7	120	-2.133163594	-2.13316125	2.13315891
8	165	-2.133163983	-2.1331631	2.13316226
Extrapolated		-2.13316418(4)	-2.1331643(6)	2.1331644(9)

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	-1.8013144780	-1.8013144780	1.8013144780
2	-2.0881998263	-2.0881998263	2.0881998263
3	-2.1285361103	-2.1285361103	2.1285361103
4	-2.1324502372	-2.1324502372	2.1324502372
5	-2.1329769612	-2.1329769612	2.1329769612
6	-2.1330922	-2.1330922	2.1330922
7	-2.1331374	-2.1331374	2.1331374
8	-2.1331539	-2.1331539	2.1331539
Extrapolated	$E_2^{(1,1)} = E_2^{(2,2)} = -E_2^{(1,2)} = 2.133165(2)$		

The extrapolated results are obtained by methods discussed in the next section. The extrapolated E_0 may be compared with Schwartz' best result of -2.1331641908.[11] The relations (24) 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, whereas the relations involving E_0 and the first-order energies are only obeyed accurately by the extrapolated results. This is obvious if we look at the expression (3) for second-order energies, using a sum over a complete set of quantum states. For any term in the infinite sum there are relations for the numerators:

$$\langle 0|T|n\rangle\langle n|V|0\rangle = \langle 0|H_0 - V|n\rangle\langle n|V|0\rangle = - |\langle 0|V|n\rangle|^2 = - |\langle 0|T|n\rangle|^2$$

since $|n\rangle$ is an eigenstate of H_0, and $|n\rangle \neq |0\rangle$.

The results of this section gives us some confidence that we have a sensible algorithm for computing second-order energies.

V. METHOD OF EXTRAPOLATION

Schwartz[31] has developed a method for estimating convergence rates of variational calculations, from an analogy with the problem of fitting a function F with N functions u_n from an orthonormal basis:

$$F \approx F_N = \sum_{n=0}^{N-1} c_n u_n$$

The mean square error is:

$$I(N) = \int |F - F_N|^2 dv = \sum_{n=N}^{\infty} c_n^2 \tag{32}$$

assuming that the expansion converges, i.e., $F = \sum_{n=0}^{\infty} c_n u_n$. For some simple one-dimensional cases with a known F and a volume element, or metric, $dv = r^a dr$, say, and using a well-behaved and smooth (infinity differentiable) system of orthonormal fitting functions that fall off exponentially at large distances, the expansion coefficients

$$c_n = \int F\, u_n\, dv$$

can be found explicitly. Schwartz shows that if F is free from singularities and smooth, then

$$c_n^2 \propto \alpha^n \quad , \qquad \alpha < 1 \tag{33}$$

This is called the fast rate of convergence. If F has a singularity at the origin, such as

$$F(r) \underset{r\to 0}{\to} \frac{1}{r^k} \; (k > 0) \qquad \text{or} \qquad F(r) \underset{r\to 0}{\to} \ln r$$

or does not fall off as fast as the fitting functions at large distances, say $F(r) \to r^{-k}$ as $r \to \infty$, or if F has some discontinuities, then

$$c_n^2 \propto \frac{1}{n^p} \tag{34}$$

If we construct a variational approximation ψ to some exact (but unknown) wavefunction Ψ, $\psi = \psi_N = \sum_{n=0}^{N-1} c_n u_n$ say, then

$$J(N) = \int (\Psi^* - \psi_N^*)(E - H)(\Psi - \psi_N)dv$$

is analogous to (32) if the operator $(E - H)dv$ is considered as some sort of generalization of the metric. If E is the exact energy of Ψ, then

$$J(N) = \int \psi_N^*(E - H)\psi_N dv = E - E_N$$

assuming ψ_N normalized, and therefore

$$J(N) - J(N + 1) = E_{N+1} - E_N \propto c_N^2$$

which follows from (32). Now take $H = H_0 + \lambda H_1$ as in (4), then $E = E_0 + \lambda E_1 + \lambda^2 E_2$ and $E_N = E_{0N} + \lambda E_{1N} + \lambda^2 E_{2N}$. Assume that the zeroth order problem (6) is solved, i.e.:

$$E_0 = E_{0N} \quad \text{and} \quad \Psi_0 = \psi_{0N}$$

then

$$J(N) = \lambda(E_1 - E_{1N}) + \lambda^2(E_2 - E_{2N})$$

using equations (6) through (10), with a subscript N on Ψ_i and E_i; $i = 0, 1, 2$.

The conclusion is therefore that we expect the differences between the computed energies for successive variational calculations, labeled by N, to be proportional to α^N or N^{-p} ($|\alpha| < 1$, $p > 1$). This should be the case, qualitatively at least, for the unperturbed energies E_0 as well as the two perturbation energies $E_1^{(i)}$ and $E_2^{(i,j)}$. The more singular the operator H is, the slower the rate of convergence (smaller p in (34)). For the one-dimensional function-fitting problems Schwartz[31] gives explicit expressions for the convergence rates, but the analogy between these model

problems and actual variational calculations is to loose to permit unambiguous predictions of the convergence rates of variational calculations. One can make educated guesses, but 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 all the singularities of Ψ built into them, one expects the fast convergence rate (33). However, even in the case of the variational calculation of the unperturbed wavefunction ψ_o for the 2^3P state, using the standard basis (18), we expect that the convergence rate will ultimately (for large ω) be slow (34), because of a weak logarithmic singularity in the "exact" wavefunction when $r_1 \to 0$ and $r_2 \to 0$ simultaneously, the so-called Fock singularity.[32] The advantage of using additional trial functions proportional to $\sqrt{r_1 + r_2}$ (Ref. 11) is that these approximate the Fock terms.

In the extrapolations in this work, we try to fit the data to both (33) and (34), the fast and slow rates. In the former case we guess the ultimate values of α 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

$$(E_\Omega - E_{\Omega-1}) \frac{\alpha}{1 - \alpha} \tag{35}$$

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 we plot the logarithm of differences between consecutively calculated energies, $\log |E_\omega - E_{\omega-1}|$, versus $\log \omega$, and try to fit the points with a straight line with more emphasis on the points with higher values of ω; the goodness

of the fit gives an indication of the usefulness of this extrapolation method. The slope of the line is p and the extrapolation is

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

where

$$F_\Omega^{+}(p) = \sum_{n=1}^{\infty}\left(\frac{\Omega}{\Omega + n}\right)^p \approx \frac{\Omega}{p - 1} - \frac{1}{2} + \frac{p}{12\Omega} - \frac{p(p + 1)(p + 2)}{720\ \Omega^3} \qquad (36a)$$

and, for the case when the differences alternate in sign:

$$F_\Omega^{-}(p) = \sum_{n=1}^{\infty}(-1)^n\left(\frac{\Omega}{\Omega + n}\right)^p \approx - \frac{1}{2} + \frac{p}{4\Omega} - \frac{p(p + 1)(p + 2)}{48\ \Omega^3} \qquad (36b)$$

The extrapolated results of Tables I and II (where the energies decreased or increased monotonically 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 results 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 ^{3}P-STATES USING THE STANDARD BASIS

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

$$H_1^{(1)} = \frac{1}{4}\alpha^2 Z\left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right)\cdot\left(\frac{\vec{r}_1 \times \vec{p}_1}{r_1^3} + \frac{\vec{r}_2 \times \vec{p}_2}{r_2^3}\right) \tag{37}$$

$$H_1^{(2)} = -\frac{3}{4}\alpha^2\left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right)\cdot\left[\frac{(\vec{r}_1 - \vec{r}_2)\times(\vec{p}_1 - \vec{p}_2)}{r_{12}^3}\right] \tag{38}$$

$$H_1^{(3)} = \frac{1}{4}\alpha^2 \frac{1}{r_{12}^3}\left(\vec{\sigma}_1\cdot\vec{\sigma}_2 - \frac{3(\vec{\sigma}_1\cdot\vec{r}_{12})(\vec{\sigma}_2\cdot\vec{r}_{12})}{r_{12}^2}\right) \tag{39}$$

$$H_1^{(4)} = -\frac{1}{2}\alpha^2 \frac{1}{r_{12}}\left(\vec{p}_1\cdot\vec{p}_2 + \frac{\vec{r}_{12}\cdot(\vec{r}_{12}\cdot\vec{p}_1)\vec{p}_2}{r_{12}^2}\right) \tag{40}$$

$$H_1^{(5)} = -\frac{1}{8}\alpha^2(p_1^4 + p_2^4) \tag{41}$$

$$H_1^{(6)} = \frac{1}{2} Z\pi\alpha^2(\delta^{(3)}(\vec{r}_1) + \delta^{(3)}(\vec{r}_2)) \tag{42}$$

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

$$H_1^{(7)} = \frac{m}{M}\vec{p}_1\cdot\vec{p}_2 \tag{43}$$

Here m is the (reduced) electron mass, $m/M \approx 1.36 \times 10^{-4}$, so the operator (43) is a somewhat more important operator than the Breit operators since $\alpha^2 = 0.54 \times 10^{-4}$. 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, $H_1^{(3)}$ 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 electrons 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[14]; the one given by Bethe and Salpeter[33] is not Hermitian. The operator $H_1^{(6)}$ has been obtained in the form (42) by Itoh[14] and Kim.[16] In this work we shall only calculate contributions when the perturbation wavefunctions $\psi_1^{(i)}$ have the same symmetry as ψ_o, i.e., from intermediate triplet P-states with odd parity. Therefore we have left out 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. 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 (18) 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 and 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_o, 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_o 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

$$\langle U_{\ell' m' n'} | H_1^{(i)} | U_{\ell mn} \rangle \qquad i = 1,2,\ldots,7$$

where $U_{\ell mn}$ is given by (18) 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 wavefunctions ψ_o (19), for $\omega = 1,2,\ldots,8$. The units are chosen for comparison with the results of Schwartz[11] and Schiff et al.[30] These results are for "stretched" states where $J = m_J = 2$. As in Section IV all calculations were done with two sets of slightly different wavefunctions ψ_o, 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 Section V has been made, the assigned errors come mostly from the uncertainties in the values of α or p used in formulas (35) or (36); this is probably too optimistic. The expectation values are in very satisfactory agreement with the results of Schwartz[11] and Schiff et al.[30] 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 Sections 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 quote the results in Appendix D. Each

Table III

Expectation values of the operators (37)-(43) using Hylleraas-expansions (18) for the wavefunctions.

ω	$E_1^{(1)}$ $(\frac{1}{2}\alpha^2$ Ry)	$E_1^{(2)}$ $(\frac{1}{2}\alpha^2$ Ry)	$E_1^{(3)}$ $(\frac{1}{2}\alpha^2$ Ry)	$E_1^{(4)}$ $(2\alpha^2$ Ry)
1	0.13621571056	-0.21827744969	0.019652745588	0.034490724822
2	0.13112509381	-0.20177641002	0.018015107575	0.032904898326
3	0.13479007901	-0.20308763420	0.017932223852	0.034113074489
4	0.13688109890	-0.20459137883	0.017982384057	0.03467268684
5	0.1378979722	-0.2053541147	0.01800112012	0.03494044683
6	0.1383407	-0.2056763	0.01800943	0.03503569
7	0.1385195	-0.20580367	0.018012740	0.035065736
8	0.1385934	-0.2058600	0.01801427	0.03507596
∞	0.13864(1)	-0.20591(1)	0.018016(1)	0.035082(2)

ω	$E_1^{(5)}$ $(2\alpha^2$ Ry)	$E_1^{(6)}$ $(2\alpha^2$ Ry)	$E_1^{(7)}$ $(2\frac{m}{M}$ Ry)
1	-9.6504742823	7.8022849193	-0.058229558253
2	-9.9742033112	7.9451810162	-0.059299556963
3	-9.9012260173	7.9053717914	-0.06196076281
4	-9.9159907956	7.9121701450	-0.06337755521
5	-9.91007660	7.908943679	-0.06419143230
6	-9.91183	7.909714	-0.06446346
7	-9.91152658	7.9095189	-0.06453566
8	-9.911905	7.909689	-0.0645629
∞	-9.91180(5)	7.90964(1)	-0.064580(5)

energy was computed by the two different methods (31), and this was done with the two slightly different wavefunctions ψ_o. There are thus 4 numbers to compare for the unmixed and 8 for the mixed second-order energies. The discrepancies between the 8 (or 4) numbers increase with ω, indicating accumulating round-off errors. One of the reasons for this may be the fact that the matrix $A_{\ell k}$ in (27) with the first row and column deleted gets close to being singular as ω increases, as mentioned in Section IV. This affects both ψ_o and $\psi_1^{(i)}$ since the matrix $A_{\ell k}$ enters the eigenvalue problem for ψ_o. Generally, the discrepancy between results calculated the same way with the two ψ_o's was slightly larger, usually one more digit, than the disagreement between the values calculated by the two different methods, using the same ψ_o. When the solutions $X_2^{(i)}$, $X_3^{(i)}$, ..., $X_{N(\omega)}^{(i)}$ were inserted into the left hand side of (27) and compared with the right hand side $b_1^{(i)}$, the numbers agreed to as many or more digits than the ones quoted in Table IV, just as in Section 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 8 values obtained for the second-order energies.

Careful extrapolations have been done, using both (35), denoted F for fast, and (36), 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

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	$E_2^{(1,1)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$	$E_2^{(2,2)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$	$E_2^{(3,3)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$	$E_2^{(1,2)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$	$E_2^{(1,3)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$
1	-0.24693997779	-0.60652019222	-0.0039149879886	0.37526345793	-0.029729889761
2	-0.36538907652	-0.79651107786	-0.0048689687195	0.51106300222	-0.039027567208
3	-0.44253234144	-0.89224182197	-0.005258842720	0.57923346960	-0.04318048113
4	-0.4894737654	-0.9507059017	-0.005438701801	0.6147659992	-0.04500565353
5	-0.52267788	-0.99038077	-0.0055549413	0.63651546	-0.04598042
6	-0.545878	-1.017182	-0.0056365	0.64920	-0.046520
7	-0.5622	-1.03632	-0.005697	0.6570	-0.04684
8	-0.5747	-1.0509	-0.005746	0.6617	-0.04705
∞	-0.61(1) F	-1.10(3) F	-0.0059(3) F	0.672(5) F	-0.0473(2) F
	-0.67(3) S	-1.15(5) S	-0.0061(1) S	0.681(5) S	-0.0476(1) S

Table IV (continued)

ω	$E_2^{(1,4)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(1,5)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(1,6)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(1,7)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{m}{M}$	$E_2^{(2,3)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{1}{4}\alpha^2$
1	-0.064385508470	-1.3529178209	0.83202422982	0.08829246019	0.048646059033
2	-0.096387812967	0.0335759747	0.1223746720	0.16006987902	0.06192418565
3	-0.11339813793	-0.1953498540	0.2630527592	0.18798596196	0.06785901636
4	-0.1227370030	-0.11532134	0.23655335	0.205644018	0.07100882584
5	-0.12846635	-0.141174	0.259488	0.21901834	0.073049241
6	-0.1315874	-0.1318	0.26125	0.225658	0.074454
7	-0.133186	-0.1270(5)	0.2629(3)	0.22829	0.07549
8	-0.134116	-0.1052(6)	0.2557(3)	0.23035	0.07629
∞	-0.1354(3) F -0.1360(5) S	-0.10(5)	0.26(3)	0.240(8) F 0.238(5) S	0.079(1) F 0.082(1) S

Table IV (continued)

ω	$E_2^{(2,4)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(2,5)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(2,6)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(2,7)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{m}{M}$	$E_2^{(3,4)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$
1	0.10839243211	2.1020269660	-1.2483005459	-0.16915204628	-0.008741807952
2	0.14564998624	-0.2939422327	-0.0090421916	-0.23587517358	-0.011210409140
3	0.16406035269	0.2955914804	-0.3217671554	-0.27157620712	-0.012264960508
4	0.1742096454	0.04485798	-0.206227866	-0.29205928	-0.01275125804
5	0.17998996	0.1445813	-0.2623536	-0.30604485	-0.012982926
6	0.182862	0.08770(4)	-0.2373	-0.312580	-0.0130910
7	0.184252	0.1216(3)	-0.2565(2)	-0.31564	-0.0131442
8	0.18502	0.1021(4)	-0.2481(2)	-0.31774	-0.013171
∞	0.1859(3) F	0.1090(6) F	-0.2508(9) F	-0.323(3) F	-0.013198(6) F
	0.1864(3) S	0.1097(1) S	-0.2513(1) S	-0.325(5) S	-0.01322(2) S

Table IV (continued)

ω	$E_2^{(3,5)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(3,6)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$E_2^{(3,7)}(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{m}{M}$
1	-0.13546082301	0.079731206176	0.013890400158
2	0.02567481126	-0.00385900032	0.018025837945
3	0.00092526288	0.009283318774	0.020086284654
4	0.007202628	0.006632136	0.02093691661
5	0.00685639	0.00708255	0.021347172
6	0.00725(3)	0.00699	0.021498
7	0.00683(5)	0.00735(3)	0.021572
8	0.00673(6)	0.00745(3)	0.021604
∞	0.0067(5)	0.0075(5)	0.02163(5) F 0.0217(1) S

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 (36a) when all ratios α are positive or in (36b) when all ratios of successive differences are negative. In Fig. 2 two examples of these plots are shown, for $E_2^{(2,5)}$ where the points fitted very nicely to a straight line and for $E_2^{(3,7)}$ where the fit was less obvious. When the spin-dependent operators are mixed with themselves and with $H_1^{(4)}$ 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 the extrapolation methods cannot be used, 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_o, 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 also $E_2^{(5,6)}$. 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_o. 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 $\vec{r}_1/r_2$ 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 $\ell = -1$ 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 5 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_o vanish when $r_{12} = 0$ (because of antisymmetry), thus that $E_2^{(1,1)}$ should converge slower than $E_2^{(2,2)}$ and $E_2^{(3,3)}$, but 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

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

which follows from the Wigner-Eckhart theorem.[34] 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

$$[E_2^{(i,j)}]_J = \sum_n{}' \frac{[\langle 0|H_1^{(i)}|n\rangle]_J[\langle n|H_1^{(j)}|0\rangle]_J}{E_0 - E_N} \tag{44}$$

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:

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

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 $\Delta\nu_{01} = (E_2)_0 - (E_2)_1$:

$$\Delta\nu_{01} = \frac{1}{2}\alpha^2 \, Ry\{\frac{1}{4}\alpha^2[3(E_2^{(1,1)} + E_2^{(2,2)} + 2E_2^{(1,2)}) - 50(E_2^{(1,3)} + E_2^{(2,3)})$$
$$+ 75\, E_2^{(3,3)}] - 2\alpha^2(E_2^{(1,4)} + E_2^{(2,4)} + E_2^{(1,5)} + E_2^{(2,5)} + E_2^{(1,6)}$$
$$+ E_2^{(2,6)}) + 30\,\alpha^2(E_2^{(3,4)} + E_2^{(3,5)} + E_2^{(3,6)})$$
$$+ 2\,\frac{m}{M}(-\,E_2^{(1,7)} - E_2^{(2,7)} + 15\, E_2^{(3,7)})\} \qquad (45)$$

and similar formulas for $\Delta\nu_{12}$ and $\Delta\nu_{02}$. In Table V we combine the two extrapolated results of Table IV to single, final values for the second-order energies. The uncertainties in the extrapolations are mostly products of human judgment (or prejudice). The contributions of these 18 corrections to the fine-structure intervals ν_{01} and ν_{12} in wavenumbers are computed from (45) and the corresponding expression for $\Delta\nu_{12}$.

As seen from Table V, many 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

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 $\Delta\nu_{01}$ 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)	0.422(2)	0.844(3)
(2,4)	0.1862(4)	-0.579(1)	-1.159(2)
(3,4)	-0.01320(2)	-0.616(1)	0.2464(4)
(1,5)	-0.10(5)	0.31(16)	0.62(31)
(2,5)	0.1095(6)	-0.341(2)	-0.681(4)
(1,6)	0.26(3)	-0.81(9)	-1.62(19)
(2,6)	-0.2512(9)	0.782(3)	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		9878.87(2)	764.241(2)

ν_{12} is not nearly so good. Clearly, the results fall short of the desired accuracy, which is to match or surpass the precision of the experimental values. But the results 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.[35] 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 increased one would probably have to use double precision arithmetic for $\omega \geq 10$, say. Although the calculations reported here were done in a matter of minutes on a CDC 6600 computer without use of tapes, 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 the next section we shall see some examples of how this leads to increased accuracy.

In Table IV each correction $E_2^{(i,j)}$ has been extrapolated separately. One might try to combine some contributions with the same J-dependence, such as $E_2^{(1,1)} + E_2^{(2,2)} + 2E_2^{(1,2)}$, for each ω and try to extrapolate the combination. Somewhat improved accuracy can in fact be achieved this way. We shall return to this question in the last section, after improved values for some of the $E_2^{(i,j)}$ have been obtained.

VII. SOME IMPROVED RESULTS, USING AN EXPANDED BASIS

We believe that the poor convergence of some of the preceding results is caused primarily by the singularities of the operators $H_1^{(i)}$, i.e., that $-(H_1^{(i)} - E_1^{(i)})\psi_o$ is not well approximated by $(H_0 - E_0)\psi_1^{(i)}$ when only standard terms (18) with $\ell \geqq 0$, $m \geqq 0$, $n \geqq 0$ are used in the expansions for $\psi_1^{(i)}$. Let us first look at a simplified problem. Take ψ_o to be just a (2p,1s) product wavefunction, let $H_1^{(1)}$ act on it and pick out the P-part:

$$\text{P-part of } H_1^{(1)}\psi_o = \text{const} \times r_1^{-3}\,\psi_o$$

where $\psi_o = \alpha(1)\alpha(2)T_1^{(1)}(\vec{r}_1)\exp(-r_1)\exp(-2r_2)$. (See Appendix B for the definition of $T_1^{(1)}(\vec{r}_1)$.) There is thus the pole term proportional to $T_1^{(1)}(\vec{r}_1)r_1^{-3}$ which will be reproduced by $H_0\psi_1^{(1)}$ if

$$\psi_1^{(1)} = \frac{1}{r_1}\,\psi_o \tag{46}$$

But with this expression for $\psi_1^{(1)}$, $H_0\psi_1^{(1)}$ will include other, less singular, terms such as $T_1^{(1)}(\vec{r}_1)\exp(-r)/r^n$ with $n = 1,2$ (and also a term $T_1^{(1)}(\vec{r}_1)\delta^{(3)}(\vec{r}_1) = 0$) which do not have any counterpart in $H_1^{(1)}\psi_o$. The solution $\psi_1^{(1)}$ of $(H_0 - E_0)\psi_1^{(1)} = -(H_1^{(1)} - E_1^{(1)})\psi_o$ might thus be a power series starting with a term like (46), but also including terms like $T_1^{(1)}(\vec{r}_1)\ln r\,\exp(-r)$, $T_1^{(1)}(\vec{r}_1)r\ln r\,\exp(-r)$ and so on, so that an exact solution for $\psi_1^{(1)}$ (which might exist if the $1/r_{12}$ term is dropped from H_0) would be rather complicated, even in this simplified case.

Turning now to the actual problem, the P-part of $H_1^{(1)}\psi_o$ is

$$\frac{1 - p_{12}}{4\pi\sqrt{2}} \sum_{\ell,m,n=0}^{\ell+m+n\leqq 0} C_{\ell mn}\, V_{\ell mn}(1,2)$$

where $V_{\ell mn}(1,2)$ is given by the expression in (B3). When $m = 0$, the first term of (B3) gives $T_1^{(1)}(\vec{r}_1)u_{\ell on}(1,2)/r_1^3$. Looking at (B1) one sees that this pole term would result from (fourth term in (B1)) $H_0 T_1^{(1)}(\vec{r}_1)u_{\ell-1\ n}(1,2)$, along with many other singular terms. This non-standard term in the expansion for $\psi_1^{(1)}$, proportional to $(1 - P_{12})T_1^{(1)}(\vec{r}_1)/r_1$, would also reproduce the terms

$$-\frac{\ell}{2}\frac{T_1^{(1)}(\vec{r}_1)\vec{r}_1\cdot\vec{r}_2}{r_1^3\ r_{12}^2}\,u_{\ell on}(1,2) \quad \text{and} \quad \frac{\ell}{2}\frac{T_1^{(1)}(\vec{r}_1)}{r_1}\,u_{\ell on}(1,2)$$

in (B3). (Use $\vec{r}_1\cdot\vec{r}_2 = \frac{1}{2}(r_1^2 + r_2^2 - r_{12}^2)$.) The two remaining terms in (B3) cause trouble when $n = 0$ in which case they are

$$\frac{\ell}{2}\frac{1}{r_2^3 r_{12}^2}\,(T_1^{(1)}(\vec{r}_1)\vec{r}_1\cdot\vec{r}_2 - T_1^{(1)}(\vec{r}_2)r_1^2)u_{\ell mo}(1,2) \tag{47}$$

The first of these can be obtained with $n = -1$ in (B1). However, this gives terms proportional to $(1 - P_{12})T_1^{(1)}(\vec{r}_1)/r_2$ in the expansion for $\psi_1^{(1)}$ which would lead an infinite value of $E_2^{(1,1)}$ if we use the algorithm of the earlier sections, since $\langle\psi_1^{(1)}|H_0|\psi_1^{(1)}\rangle$ includes integrals with r_2^{-3} in the integrand, coming from the $-2/r_2$ term in H_0. Finally, to obtain the second term of (47), one would need terms like $(1 - P_{12})T_1^{(1)}(\vec{r}_2)u_{\ell m-1}(1,2)$ in the expansion for $\psi_1^{(1)}$. Thus it would be a rather hopeless task to reproduce all the terms of $H_1^{(1)}\psi_o$ by adding more and more special terms to the expansion for $\psi_1^{(1)}$. Even if one managed to do this, there would be very many terms in $H_0\psi_1^{(1)}$ without counterpart in $H_1^{(1)}\psi_o$. Now all but the first term in (B3) are proportional to $\vec{r}_1 \times (\vec{r}_1 \times \vec{r}_2)$ and only contribute an exchange part to the matrix elements of $H_1^{(1)}$, these are generally smaller than the direct part because the latter involves folding radial functions (like $r_1 \exp(-\frac{1}{2}\kappa r_1)$ and $r_1 \exp(-\frac{1}{2}\kappa r_1)$) with coinciding peaks, whereas the former involves

folding of functions (like $r_1 \exp(-\frac{1}{2}\kappa r_1)$ and $\exp(-\frac{1}{2}\kappa\sigma r_1)$) with maxima occurring for different values of the argument. Therefore we shall only include terms in $\psi_1^{(1)}$ which will give the leading singularities in $H_1^{(1)}\psi_o$, which are the terms proportional to $T_1^{(1)}(\vec{r}_1)/r_1^3$. The following extended expansion for $\psi_1^{(1)}$ is used, see (18):

$$\psi_1^{(1)} = \sum_{n=0}^{\omega} x_n^{(1)} U_{0-1\ n} + \sum_{\ell,m,n=0}^{\ell+m+n\leq\omega} X_{\ell mn}^{(1)}\, U_{\ell mn} \tag{48}$$

Powers of r_{12} in the new terms have been dropped, their inclusion would increase the number of new terms from $\omega + 1$ to $\frac{1}{2}(\omega + 1)(\omega + 2)$ while adding little more flexibility. The new terms approximate the behavior of $\psi_1^{(1)}$ as $r_1 \to 0$ $(r_2 \to 0)$ in which case $r_{12} \to r_2$ $(r_{12} \to r_1)$. The expansion (48) does not lead to many new integrals, and most of the subroutines written for the earlier calculations can still be used.

It follows from the work of Schwartz[31] that the convergence of the second-order energies should improve when additional trial terms, reflecting the singularities of $H_1^{(i)}$, are introduced in the expansions for $\psi_1^{(i)}$. If one tries to fit a function $F \to r^{-d}$ as $r \to 0$ with functions that are regular at the origin, corresponding to fitting $\psi_1^{(i)}$ with standard terms, the convergence rate for the one-dimensional model problem where the volume element is $dv = r^a dr$ is (see Section V):

$$c_n^2 \sim 1/n^{a-2d+2} \qquad \text{(Ref. 31)}$$

The additional terms in (48) should change d from 1 to 0, so that a significant improvement of the convergence of $E_2^{(1,1)}$ should occur. However, there may still be singularities, possibly logarithmic ones, to slow down the convergence.

Denoting the non-standard terms in (48) by V_n and the standard ones by U_k, the system of equations for $\psi_1^{(i)}$ is now:

$$\sum_{n=1}^{\omega+1} \tilde{A}_{\ell n} x_n^{(i)} + \sum_{k=1}^{N(\omega)} \tilde{A}_{\ell k} X_k^{(i)} = B_\ell^{(i)} \tag{49}$$

$$\ell = 1,2,\ldots,N(\omega)+\omega+1$$

where $N(\omega)$ is given by (20) and

$$B_\ell^{(i)} = - \langle V_\ell | H_1^{(i)} - E_1^{(i)} | \psi_o \rangle \tag{50}$$

$$\ell = 1,2,\ldots,\omega+1$$

and

$$B_\ell^{(i)} = b_{\ell-\omega-1}^{(i)} \qquad \ell = \omega+2,\omega+3,\ldots,N(\omega)+\omega+1$$

with $b_\ell^{(i)}$ given by (28). Explicitly the matrix $\tilde{A}$ in (49) is:

$$\tilde{A} = \left| \begin{array}{c|c} \langle V_{n'} | H_0 - E_0 | V_n \rangle & \langle V_{n'} | H_0 - E_0 | U_k \rangle \\ \hline \langle U_{k'} | H_0 - E_0 | V_n \rangle & \langle U_{k'} | H_0 - E_0 | U_k \rangle \end{array} \right| \tag{51}$$

$$n',n = 1,2,\ldots,\omega+1$$

$$k',k = 1,2,\ldots,N(\omega)$$

We first tried to solve the system (49) as it stands, without deleting any of the equations. In principle the matrix $\tilde{A}$ is non-singular; E_0

has a value which makes the lower right hand block in (51) singular, but this should not stop $\tilde{A}$ from having rank equal to its dimension $N(\omega)+\omega+1$. However, this leads to quite unreasonable results, the second-order energies came out as huge numbers. The reason for this is probably that $\tilde{A}$ is quite close to being singular. After some experimentation it was decided to adjust E_0 in (51) to the lowest value which makes $\tilde{A}$ singular. This number, call it $\tilde{E}_0$, is of course the smallest eigenvalue of H_0 in the enlarged basis $(V_1,\ldots,V_{\omega+1}, U_1,\ldots,U_{N(\omega)})$. An adjustment of $E_1^{(i)}$ in (50) and (28) must also be made, otherwise the equations (49) will be overdetermined after E_0 has been changed to $\tilde{E}_0$. The elements of the eigenvector $\tilde{\psi}_o$ of $\tilde{A}$ corresponding to $\tilde{E}_0$ demonstrate the linear dependence among the rows of $\tilde{A}$ (see page 20), thus $E_1^{(i)}$ must be adjusted to $\tilde{E}_1^{(i)}$ determined by

$$0 = \langle\tilde{\psi}_o|H_1^{(i)} - \tilde{E}_1^{(i)}|\psi_o\rangle \tag{52}$$

so that, explicitly:

$$\tilde{E}_1^{(i)} \times \langle\tilde{\psi}_o|\psi_o\rangle = \sum_{m=1}^{N(\omega)} C_m [\sum_{n=1}^{\omega+1} \tilde{c}_n \langle V_n|H_1^{(i)}|U_m\rangle + \sum_{k=1}^{N(\omega)} \tilde{C}_k \langle U_k|H_1^{(i)}|U_m\rangle]$$

and a similar expression for $\langle\tilde{\psi}_o|\psi_o\rangle$. Here $(\tilde{c}_1,\ldots,\tilde{c}_{\omega+1}, \tilde{C}_1,\ldots,\tilde{C}_{N(\omega)})$ is the eigenvector $\tilde{\psi}_o$. One can now delete any one of the $N(\omega)+\omega+1$ equations (49), but we choose to put $X_1^{(i)} = 0$ and drop the $(\omega+2)^{th}$ equation in (49), so that the $(\omega+2)^{th}$ row and column of $\tilde{A}$ in (51) are deleted. This choice is made for the reasons stated in Section IV (pages 20 and 21); the first standard term in the expansion for $\tilde{\psi}_o$ is the most important one, corresponding to a (1s,2p) wavefunction. Finally, $E_2^{(i,j)}$ is given by

$$E_2^{(i,j)} \times \langle\psi_o|\psi_o\rangle = \langle\psi_o|H_1^{(i)} - \tilde{E}_1^{(i)}|\psi_1^{(j)}\rangle = - \langle\psi_1^{(i)}|H_0 - \tilde{E}_0|\psi_1^{(j)}\rangle$$

$\tilde{E}_1^{(i)}$ must be used in this formula rather than $E_1^{(i)}$, because if $E_1^{(i)}$ is used $E_2^{(i,j)}$ will change if an arbitrary multiple of $\tilde{\psi}_o$, the solution of

the homogeneous equation corresponding to the inhomogeneous equation for $\psi_1^{(i)}$, is added to $\psi_1^{(i)}$. Using $\tilde{E}_1^{(i)}$ the resulting $E_2^{(i,j)}$ is unique in this sense.

This provides an algorithm resembling the one used in Sections IV and VI, but in addition to ψ_o (E_0 is not required) one also needs $\tilde{E}_0$ and $\tilde{\psi}_o$ as input. These are found by the iterative method used to determine E_0 and ψ_o, described in Appendix C. In Table VI we give the results for $E_2^{(1,1)}$ calculated by this method, using the expansion (48) for $\psi_1^{(1)}$. They represent a significant improvement over the corresponding results from Table IV. Since the ratio of successive differences was rather constant (ranging from 0.45 to 0.52 for $2 \leq \omega \leq 8$), only the fast extrapolation has been used. The eigenvalues $\tilde{E}_0$ were rather close to E_0, they agreed to four digits for $\omega = 1$ and 2, to six digits for $\omega = 3$, 4 and 5, to seven digits for $\omega = 6$ and 7, and to eight digits for $\omega = 8$. The differences between $\tilde{E}_1^{(1)}$ and $E_1^{(1)}$ were greater, ranging from two digits of agreement for $\omega = 1,..,6$ to four digits for $\omega = 7$ and 8.

Consider $E_2^{(1,6)}$ next. Since

$$H_1^{(6)}\psi_o = \alpha^2 \frac{1 - P_{12}}{4\sqrt{2}} \delta^{(3)}(\vec{r}_2) \sum_{\ell,m=0}^{\ell+m\leq\omega} C_{\ell mo} T_1^{(1)}(\vec{r}_1) r_1^{m+\ell} e^{-\frac{\kappa\sigma}{2} r_1}$$

we see that additional terms in $\psi_1^{(6)}$ proportional to $T_1^{(1)}(\vec{r}_1)/r_2$ will produce $\delta^{(3)}(\vec{r}_2)$ when acted upon by H_0; in addition to other, less singular terms that are undesirable but cannot be avoided. Thus we use the following extended expansion for $\psi_1^{(6)}$, similar to (48):

$$\psi_1^{(6)} = \sum_{m=0}^{\omega} x_m^{(6)} U_{0m-1} + \sum_{\ell,m,n=0}^{\ell+m+n\leq\omega} X_{\ell mn}^{(6)} U_{\ell mn} \tag{53}$$

Table VI

The second-order energy $E_2^{(1,1)}$ calculated with the expansion (48) for $\psi_1^{(1)}$.

ω	Number of terms in $\psi_1^{(1)}$	$E_2^{(1,1)}(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$
1	6	-0.51197398824
2	13	-0.56885476328
3	24	-0.61688183482
4	40	-0.6401105462
5	62	-0.6522232
6	91	-0.658084
7	128	-0.660772
8	174	-0.662040
∞		-0.6632(2) F

Table VII

The second-order energy $E_2^{(1,6)}$ calculated with the expansions (48) for $\psi_1^{(1)}$ and (53) for $\psi_1^{(1)}$.

ω	$E_2^{(1,6)}(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$
2	0.27078605763
3	0.26328428177
4	0.2686979553
5	0.27067971
6	0.272784
7	0.27308
8	0.27315(16)
∞	0.2732(3)

The matrix of $\langle\psi_1^{(6)}|H_0 - \tilde{E}_0|\psi_1^{(1)}\rangle$ is then no longer symmetric. Denoting the additional terms in (53) by W_n, the matrix $\tilde{A}$ of $H_0 - \tilde{E}_0$ to be used when solving $(H_0 - \tilde{E}_0)\psi_1^{(1)} = -(H_1^{(1)} - E_1^{(1)})\psi_o$ is no longer given by (51); the two blocks in the lower left and right hand corners are unchanged, but the block in the upper left hand corner is $\langle W_{n'}|H_0 - \tilde{E}_0|V_n\rangle$ and the one in the upper right hand corner is $\langle W_{n'}|H_0 - \tilde{E}_0|U_k\rangle$. One must now distinguish between the left and right eigenvectors $\tilde{\psi}_o^\ell$ and $\tilde{\psi}_o^r$ of H_0 in this extended, mixed representation, corresponding to $\tilde{E}_0$. (For a symmetric matrix these are equal.) In (52), the value of $\tilde{E}_1^{(1)}$ was determined by multiplication from the left, so that:

$$\tilde{E}_1^{(1)} = \langle\tilde{\psi}_o^\ell|H_1^{(1)}|\psi_o\rangle/\langle\tilde{\psi}_o^\ell|\psi_o\rangle$$

With these modifications we calculate $E_2^{(6,1)}$. Notice that the matrix elements of $H_1^{(1)}$ $(H_1^{(6)})$ between the new and the standard terms are $\langle W_n|H_1^{(1)}|U_k\rangle$ $(\langle U_k|H_1^{(6)}|V_n\rangle)$ where W_n (V_n) are the new terms introduced to reflect the singularity of $H_1^{(6)}$ $(H_1^{(1)})$; this is evident from the variational functional (14). To calculate $E_2^{(1,6)}$ (see (11) and (13) for the precise definition of $E_2^{(i,j)}$) one solves (49) for $\psi_1^{(6)}$, but where the matrix $\tilde{A}$ is the transpose of the one used in solving for $\psi_1^{(1)}$. Furthermore:

$$\tilde{E}_1^{(6)} = \langle\psi_o|H_1^{(6)}|\tilde{\psi}_o^r\rangle/\langle\psi_o|\tilde{\psi}_o^r\rangle$$

So we have a slightly more complicated algorithm for calculating $E_2^{(1,6)}$ and $E_2^{(6,1)}$. No new integrals were required and $\tilde{\psi}_o^r$, $\tilde{\psi}_o^\ell$ and $\tilde{E}_0$ were found by the method of Appendix C. For $\omega = 1$ (6-dimensional matrix) the iterations did not converge, so there are no results for $\omega = 1$. In Table VII the values for $\omega = 2,\ldots,8$ are given, $E_2^{(1,6)}$ and $E_2^{(6,1)}$ agreed to the digits quoted. The differences between calculated results behave rather erratically with ω, but they are quite small, so we have

just guessed at the final value, with a generous uncertainty. For $\omega = 2$ only the two first digits of E_0 and $\tilde{E}_0$ were equal, but $|E_0 - \tilde{E}_0|$ decreased with ω; for $\omega = 7$ and 8 there was 6 digits of agreement. For $\tilde{E}_1^{(1)}$ (distinct from the $\tilde{E}_1^{(1)}$ used in calculating $E_2^{(1,1)}$) and $\tilde{E}_1^{(6)}$, the number of digits that agreed with $E_1^{(1)}$ and $E_1^{(6)}$ of Table III ranged from 2 to 4 with increasing ω.

Finally, we try two different expansions for $\psi_1^{(2)}$ and $\psi_1^{(3)}$. The operators $H_1^{(2)}$ and $H_1^{(3)}$ are singular when $r_{12} \to 0$, and from (B4) and (B5) it is seen that $H_1^{(i)}\psi_o$ contains terms proportional to $1/r_{12}^3$ when $\ell = 0$ $(i = 2,3)$. Similar terms are obtained from $H_0\psi_1^{(i)}$ if functions proportional to $1/r_{12}$ are included in $\psi_1^{(i)}$. This should take care of the dominant singularities that slow down the convergence of $E_2^{(2,2)}$, $E_2^{(3,3)}$ and $E_2^{(2,3)}$, although terms with $\ln r_{12}$ should probably also be included. We try two simple expansions:

$$\psi_1^{(i)} = \sum_{n=0}^{\omega} x_n^{(i)} U_{-10n} + \sum_{\ell,m,n=0}^{\ell+m+n\leq\omega} X_{\ell mn}^{(i)} U_{\ell mn} \tag{54}$$

$$\psi_1^{(i)} = \sum_{m=0}^{\omega} x_n^{(i)} U_{-1m0} + \sum_{\ell,m,n=0}^{\ell+m+n\leq\omega} X_{\ell mn}^{(i)} U_{\ell mn} \tag{55}$$

A better expansion would include terms U_{-1mn} with $m \geqq 0$, $n \geqq 0$ and $m + n \leqq \omega$, but it is desirable, from a practical point of view, to keep the number of extra terms small. The operator $H_1^{(4)}$ is also singular when $r_{12} = 0$, but from (B6) it is seen that all terms in $H_1^{(4)}\psi_o$ with $1/r_{12}^3$ are proportional to $(r_1^2 - r_2^2)/r_{12}^3$ when $\ell = 0$. The angular average of $(r_1^2 - r_2^2)/r_{12}^3$ is equal to that of $1/r_{12}$, so that an expansion like (54) or (55) is not required for $\psi_1^{(4)}$. Nevertheless we calculate $E_2^{(2,4)}$, $E_2^{(3,4)}$ and $E_2^{(4,4)}$ along with $E_2^{(2,2)}$, $E_2^{(3,3)}$ and $E_2^{(2,3)}$ with both the expansions (54) and (55) for $\psi_1^{(i)}$, $i = 2,3,4$. No more work (calculation

of integrals) is involved for the three energies $E_2^{(i,4)}$ $(i = 2,3,4)$ once $E_2^{(2,2)}$, $E_2^{(3,3)}$ and $E_2^{(2,3)}$ are done. These six second-order energies are computed by the same algorithm that was used to compute $E_2^{(1,1)}$. One could also use a mixed representation, say (54) for $\psi_1^{(i)}$ and (55) for $\psi_1^{(j)}$ $(i,j = 2,3,4)$ and compute $E_2^{(i,j)}$ by the method used for $E_2^{(1,6)}$. Some additional integrals are required for the matrix element of H_0 and $H_1^{(i)}$ between standard terms and the functions with $1/r_{12}$ and of H_0 with new terms on both sides. Great care is required in the evaluation of these integrals since they are divergent unless certain combinations are taken. This is described in Appendix A. It is interesting to note that the matrix of H_0 is no longer automatically symmetric; denoting the additional terms in (54) or (55) by V_n:

$$\int d^3\vec{r}_1(V_n^*\nabla_1^2 V_m - V_m^*\nabla_1^2 V_n) = \int_{\text{surface}} d\vec{\sigma}_1\cdot(V_n^*\nabla_1 V_m - V_m^*\nabla_1 V_n)$$

The surface integral over the far-away surface vanishes as usual, but there is also an integral over a small spherical surface of radius ϵ, say, surrounding the singularity at $r_{12} = 0$. It turns out that this contribution vanishes because of the angular integration, but the integrand does not go to zero as $\epsilon \to 0$. For the same reason there is never any contribution to the matrix elements of H_0 from a δ-function $\delta^{(3)}(\vec{r}_{12})$ resulting from the action of H_0 on V_n.

In Table VIII we give some of the results of these calculations. For the unmixed energies $E_2^{(i,i)}$ what we compute is always an upper bound (see Appendix D for a formal proof of this statement), therefore we have only quoted the results for $E_2^{(i,i)}$ $(i = 2,3)$ when the expansion (54) was used for $\psi_1^{(i)}$ since these were slightly smaller (larger in magnitude) than the values obtained with (55). The extrapolated results from both sets of calculations (using (54) and (55)) were the same for $E_2^{(2,2)}$,

Table VIII

Second-order energies calculated with the expansion (54) for $\psi_1^{(i)}$, $i = 2,3$.

ω	$E_2^{(2,2)}(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(3,3)}(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(2,3)}(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$
1	-0.8857638070	-0.005239656190	0.067865863045
2	-0.9922391306	-0.005741438702	0.074763980404
3	-1.0544582922	-0.005931330644	0.078126662368
4	-1.0870891287	-0.006006971263	0.0796813108
5	-1.1049002	-0.006033454	0.08036593
6	-1.11637	-0.00604915	0.080787
7	-1.12170	-0.00605681	0.080985
8	-1.12623	-0.00606316	0.081148
∞	-1.143(5) S	-0.006085(5) S	0.0817(2) S

$E_2^{(3,3)}$ and $E_2^{(2,3)}$. In the latter case, the calculated numbers obtained with (54) were slightly closer to the extrapolated results than the ones from (55), for the higher values of ω, so again only the results from (54) are quoted. For $\omega = 8$, the values obtained using (55) were: $E_2^{(2,2)} = -1.12280$, $E_2^{(3,3)} = -0.006057$ and $E_2^{(2,3)} = 0.08100$. The results obtained for $E_2^{(2,4)}$, $E_2^{(3,4)}$ (and $E_2^{(4,4)}$), using both (54) and (55) for $\psi_1^{(i)}$ $(i = 2,3,4)$, were virtually the same as the ones obtained from the standard basis; the extrapolated values were in complete agreement with the results of Table IV and V, with just as big uncertainties, so there is no point in quoting these numbers. It is not surprising that the expansions (54) and (55) should give essentially the same results since the non-standard terms approximate the behavior of $\psi_1^{(i)}$ at $r_{12} \approx 0$ where $r_1 \approx r_2$. One could probably not expect any significant improvement in the fairly accurate results of Table IV for $E_2^{(2,4)}$ and $E_2^{(3,4)}$. In the variational functional (14) for $E_2^{(i,j)}$ $\psi_1^{(2)}$ or $\psi_1^{(3)}$ is improved when (54) or (55) is used rather than just standard terms, but this is not true for $\psi_1^{(4)}$. Since one of the two perturbed wavefunctions in (14) is improved one might have anticipated a slight improvement. The differences between E_0 and $\tilde{E}_0$ as well as between $E_1^{(i)}$ and $\tilde{E}_1^{(i)}$ $(i = 2,3,4)$ were of the same orders of magnitude (for $\omega = 1,2,\ldots,8$) as the corresponding quantities in the calculation of $E_2^{(1,1)}$ reported on page 47.

The results of Table VI, VII and VIII are in excellent agreement with the corresponding results from Tables IV and V, and we have achieved a significant improvement in accuracy with only a few extra trial functions. In fact, the values for $E_2^{(1,1)}$, $E_2^{(1,6)}$ and $E_2^{(3,3)}$ were improved by two orders of magnitude and $E_2^{(2,2)}$ and $E_2^{(2,3)}$ were improved by one order. This lends further confidence to the computer algorithms used as well as to the extrapolation schemes. The calculations of this section

were not repeated with slightly perturbed ψ_o's and $\tilde{\psi}_o$'s (resulting from one more iteration of the procedure of Appendix C), except for the results of Table VIII for $\omega = 1,2,3$ and 4. With once-more-iterated $\tilde{\psi}_o$'s, but the same ψ_o's, numbers were obtained that agreed with those of Table VIII to seven digits. However, in view of the fact that the extrapolated results were equal when different expansions ((54) and (55)) were used for $\psi_1^{(i)}$ $(i = 2,3,4)$ and of the fairly quick converge of the five result obtained here, we do not believe that a slight variation in $\tilde{\psi}_o$ (or ψ_o) would change any of the extrapolated results of this section.

VIII. SUMMARY AND CONCLUSION

To obtain the best possible values for the 18 second-order energies from the calculations reported in this work, we add $E_2^{(3,5)}$ and $E_2^{(3,6)}$ of Table IV for each of the five highest values of ω and extrapolate the sum, as mentioned at the end of Section VI. The same was done for $E_2^{(1,7)} + E_2^{(2,7)}$, and the results given in Table IX. The final results have just been guessed, but there is an improvement in accuracy over the values of Table V. We also tried to use formulas like (45) for each value of ω and to extrapolate $\Delta\nu_{01}$ or $\Delta\nu_{02}$, but this did not prove profitable. In Table X we list the contributions of the five improved results of Section VII and of the final values from Table IX to the fine-structure intervals ν_{01} and ν_{02}. Half of the 18 second-order contributions to the larger fine-structure interval ν_{01} are now sufficiently accurate, i.e., the uncertainty in their perturbation of the interval is less than 1 ppm of the interval itself, or less than 0.01×10^{-4} cm^{-1}. The ones that pass the test are the five results from Section VII and $E_2^{(1,3)}$, $E_2^{(2,4)}$ and $E_2^{(3,4)}$ of Table V. Of the remaining 9 contributions only $E_2^{(1,5)}$ is really inaccurate. $E_2^{(1,2)}$ and $E_2^{(3,7)}$ are borderline cases, $E_2^{(2,5)}$ and $E_2^{(2,6)}$ are quite good if one believes the extrapolation, but the fact that one was able to extrapolate so accurately may be accidental (see page 37). If the results of Table IX are taken at face value, the contributions of $(E_2^{(3,5)} + E_2^{(3,6)})$ and $(E_2^{(1,7)} + E_2^{(2,7)})$ to ν_{01} are also sufficiently accurate. Adding all the contributions except the one from $E_2^{(1,5)}$ we get

$$\Delta\nu_{01} = 1.38(2) \times 10^{-4} \text{ cm}^{-1}$$

The situation for the smaller interval ν_{12} is not nearly so good, because the contributions are required to an absolute accuracy of 0.001×10^{-4} cm^{-1},

Table IX

Combination of some results from Table IV with the same spin-dependence.

ω	$2(E_2^{(3,5)} + E_2^{(3,6)})$ $(\frac{1}{2}\alpha^2\ \mathrm{Ry})\alpha^2$	$2(E_2^{(1,7)} + E_2^{(2,7)})$ $(\frac{1}{2}\alpha^2\ \mathrm{Ry})\frac{m}{M}$
4	0.0276695	-0.17283054
5	0.027877	-0.1740530
6	0.02849(7)	-0.173843
7	0.02836(4)	-0.17471(1)
8	0.02833(3)	-0.17478
∞	0.0283(3)	-0.1745(7)

Table X

Contributions of the improved values for some second-order energies to the fine-structure intervals.

Second-order energy	Final result from Sec. VII or Table IX	Contribution to $\Delta\nu_{01}$ in 10^{-4} cm^{-1}	Contribution to $\Delta\nu_{12}$ in 10^{-4} cm^{-1}
$E_2^{(1,1)}$	-0.6632(2)	-0.7738(2)	0
$E_2^{(2,2)}$	-1.143(5)	-1.333(6)	0
$E_2^{(2,3)}$	0.0817(2)	-1.589(4)	0.2542(6)
$E_2^{(3,3)}$	-0.006085(5)	-0.1775(1)	0.05680(5)
$E_2^{(1,6)}$	0.2732(3)	-0.8500(9)	-1.700(2)
$2(E_2^{(3,5)} + E_2^{(3,6)})$	0.0283(3)	0.660(7)	-0.264(3)
$2(E_2^{(1,7)} + E_2^{(2,7)})$	-0.1745(7)	0.694(3)	1.388(6)

or one order of magnitude better than for ν_{01}, to match the experimental value. Of the 15 contributions to $\Delta\nu_{12}$ in Tables V and X, only those from $E_2^{(2,3)}$, $E_2^{(3,3)}$, $E_2^{(1,3)}$ and $E_2^{(3,4)}$ are sufficiently accurate.

It should not take much more effort to obtain the required accuracy for all the contributions to $\Delta\nu_{01}$. Using a mixed representation with expansion (48) for $\psi_1^{(1)}$ and (54) for $\psi_1^{(2)}$ to calculate $E_2^{(1,2)}$ by the method used for $E_2^{(1,6)}$ in Section VI will probably give sufficiently accurate results. The same goes for $E_2^{(2,6)}$ and $E_2^{(3,6)}$, these can be done as $E_2^{(1,6)}$ but with expansion (54) for $\psi_1^{(2)}$ and $\psi_1^{(3)}$. Since $H_1^{(7)}$ is not more singular than H_0 it might be sufficient to use just a truncated standard expansion for $\psi_1^{(7)}$ and (54) or (48) for $\psi_1^{(1)}$, $\psi_1^{(2)}$ and $\psi_1^{(3)}$ to obtain better values for $E_2^{(1,7)}$, $E_2^{(2,7)}$ and $E_2^{(3,7)}$. When the number of terms in the expansions for $\psi_1^{(i)}$ and $\psi_1^{(j)}$ are different functions of ω it becomes necessary to truncate one of the expansions after an "unnatural" number of terms so that the two expansions have the same dimension; otherwise the matrix $\tilde{A}$ in (51) will not be square. If standard terms prove inadequate for $\psi_1^{(7)}$ it is probably because $H_1^{(7)}$ and H_0 have different angular behavior. It was found that to reproduce the angular dependence of $H_1^{(7)}\psi_0$ non-standard terms like $U_{\ell mn} \cos \theta_{12}$ with m or n (or both) zero, in addition to the standard ones, should be included in the expansion for $\psi_1^{(7)}$. This was used to calculate $E_2^{(7,7)}$; the results obtained were slightly better than those of Table XI in Appendix D. Lastly, in the expansion for $\psi_1^{(5)}$ one has to include (at least) non-standard terms like those in both (48) and (53); we tried using (48) for $\psi_1^{(1)}$ and just (53) for $\psi_1^{(5)}$, but the results for $E_2^{(1,5)}$ were poor. We regret that we did not have time to carry out these computations, since most of the programming required has already been done. The second-order perturbations when $\psi_1^{(1)}$, $\psi_1^{(2)}$ and $\psi_1^{(3)}$ have symmetries other than triplet P, i.e.,

singlet P and D and triplet D and F (see page 29) also remains to be calculated, this will require more work.

However, to match the experimental value of the smaller fine-structure interval ν_{12} one would have to push the accuracy one order of magnitude further, this would probably require substantially more effort. One could try to use the methods presented here for very much larger dimensions, which would take a lot of computer time, or one could try to make the trial functions more flexible by including terms with $\ln r_1$, $\ln r_2$ and $\ln r_{12}$ in the expansions, and possibly also functions that reflect the angular dependence of the operators. This would lead to many new classes of integrals which would have to be evaluated.

Finally, it must be said that there is always the possibility of some undetected errors in the extensive computer programs written for this work. We have performed every test we could think of; the integrals were evaluated in more than one way whenever possible, and the matrices of all eight operators were checked for symmetry. (This gives a useful test, see Appendix B.) The results themselves are reasonable, and our values for the nonrelativistic energy of the 2^3P state in helium as well as for the expectation values of the seven perturbing operators are in excellent agreement with the results of other investigators. But the best check of all is for someone else to repeat these calculations independently. This seems worthwhile in view of the fact that the present work is one of the necessary steps required for a new high-precision determination (from ν_{01}) of the fine-structure constant.

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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[11] and Hambro.[27]

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

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

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

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

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

which follows from

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos\theta_{12} \quad \text{(A2)}$$

and

$$B(L,M,N) = \frac{L-2}{L+2}[B(L-2,M+2,N) + B(L-2,M,N+2) - 2A(L-2,M+1,N+1)] \quad \text{(A3)}$$

which follows from (A2) and

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

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

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

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

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

where the F-integrals are defined by

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

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:

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

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

which follows after one partial integration in s. The equations (A5) and (A6) follow from

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

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

These recursion schemes give the A-integrals for $L \geq 1$, $M \geq 1$, $N \geq 1$ and the B-integrals for $L \geq 1$, $M \geq 2$, $N \geq 2$. 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 $L \geq 4$ 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

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

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:

$$FL(M,N;\alpha,\beta) = \int_0^1 dx\, x^{M-1} \ln\frac{1+x}{1-x} \int_0^\infty dy\, y^{M+N-1}\, e^{-(\alpha x+\beta)y}$$

$$= \frac{(M+N-1)!}{\alpha^{M+N}} \int_0^1 dx\, \frac{x^{M-1} \ln\frac{1+x}{1-x}}{(x+\frac{\beta}{\alpha})^{M+N}}$$

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

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

To avoid dangerous recursion schemes we compute the integrals along $M + N =$ constant and use the backwards recursion formula

$$FL(M,N;\alpha,\beta) = \frac{\alpha FL(M+1,N;\alpha,\beta) + \beta FL(M,N+1;\alpha,\beta)}{M+N} \tag{A7}$$

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

For $\alpha = \beta$, we have

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

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. Define 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 Eulers B-function.

$$J(M,N) = - \frac{\partial}{\partial M} \frac{\Gamma(M)\Gamma(N)}{\Gamma(M + N)} = - \frac{\Gamma(M)\Gamma(N)}{\Gamma(M + N)} \left(\frac{\Gamma'(M)}{\Gamma(M)} - \frac{\Gamma'(M + N)}{\Gamma(M + N)}\right)$$

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

where γ is Eulers constant.[36] Thus

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

and we obtain a closed expression:

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

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

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

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

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

$$FL(M,N;\kappa,\kappa\sigma) = \frac{1}{A^{M+N}} \sum_{k=0}^{\infty} \left[\sum_{J=1}^{N} FJ(J)FJK(J,k)SKJ(J,k)\right]$$

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

$$FJ(J) = 2^J(N-1)!(M+N-J-1)!/(N-J)!$$

$$FJK(J,k) = B^k J(J+1)\ldots(k+J-1)/k! \qquad \text{for} \qquad k \geqq 1$$

$$FJK(J,0) = 1$$

$$SKJ(J,k) = \frac{1}{k+J} + \ldots + \frac{1}{k+M+N-1}$$

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 $k-1$ first terms fall 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:

$$\frac{1}{(1 - u + \frac{1}{\sigma}(1 + u))^L} = (\frac{\sigma}{2})^L[1 + \sum_{k=1}^{\infty} \frac{B^k(1-u)^k}{k!} L(L+1)\ldots(L+k-1)]$$

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

$$FJK(J,k) = B^K(M+N-J)\ldots(M+N-J+k-1)/k! \qquad \text{for} \qquad k \geqq 1$$

$$FJK(J,1) = 1\ , \qquad SKJ(J,k) = \frac{1}{J} + \ldots + \frac{1}{k+M+N-1}$$

and $FJ(J)$ is unchanged.

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

$$ADI(0,M,N) = \frac{1}{2}(FL(M,N;\kappa\sigma,\kappa) + FL(N,M;\kappa,\kappa\sigma))$$

$$\begin{aligned} BDI(0,M,N) = \frac{1}{4}(&FL(M+1,N-1;\kappa\sigma,\kappa) + FL(M-1,N+1;\kappa\sigma,\kappa) \\ &+ FL(N+1,M-1;\kappa,\kappa\sigma) + FL(N-1,M+1;\kappa,\kappa\sigma)) \\ &- \frac{1}{2}(F(M,N;\kappa\sigma,\kappa) + F(N,M;\kappa,\kappa\sigma)) \end{aligned}$$

and similar formulas for $AEX(0,M,N)$ and $BEX(0,M,N)$.

We also require the A and B integrals for $M = 0$, $N \geqq 1$ and $M \geqq 1$, $N = 0$ when $L \geqq 1$. 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:

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

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

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

and start 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

$$F(M,0;\alpha,\beta) = \sum_{k=0}^{n} \frac{(-1)^k (M-k-2)!k!}{(\alpha+\beta)^{M-k-1}\beta^{k+1}} + r_n \tag{A10}$$

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 $n \leqq M-3$. 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 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[29] we obtained

$$F(50,0;\kappa\sigma,\kappa) = 0.2702036705 \times 10^{23}$$

$$F(50,0;\tfrac{1}{2}\kappa(1+\sigma),\tfrac{1}{2}\kappa(1+\sigma)) = 0.413306 \times 10^{23}$$

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 8 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

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

and by truncating an infinite series:

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

$$I(M) = \int_0^\infty dr\, e^{-\kappa r} r^{M-1}\ln r = \frac{M-1}{\kappa} I(M-1) + \frac{(M-2)!}{\kappa^M}$$

and $I(1) = -(\ln\kappa + \gamma)/\kappa$. It turns out that Eulers 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 9 digits:

$$F(50,0;\kappa,\kappa\sigma) = 0.880736751 \times 10^{23}$$

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 $M+N \geqq 1$) 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[37] which is well suited to these cases where the integrand has mild singularities at both endpoints. First, set $u = 1/(1+\exp(-y))$ to transform the region of integration from $0 \leqq u \leqq 1$ to $-\infty \leqq y \leqq \infty$ 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.

This concludes the description of the methods used to evaluate all integrals required for the matrix elements of the eight operators in the standard basis.

To calculate $E_2^{(1,1)}$ and $E_2^{(1,6)}$ with the extended expansions (48) and (53) for $\psi_1^{(1)}$ and $\psi_1^{(6)}$, respectively, we need integrals $A(L,M,N)$ with $M = 0$ or $N = 0$ ($L \geqq 1$) and $B(L,M,N)$ with $M = -1$ and $M = 0$ (or $N = -1,0$). These are evaluated from $F(M,N)$ integrals with $N = -1$ and $N = -2$, since we already have calculated $F(M,0)$-integrals, the new integrals are easily obtained by using formula (A8).

When the expansions (54) or (55) are used for $\psi_1^{(2)}$, $\psi_1^{(3)}$ or $\psi_1^{(4)}$, one runs into integrals with $(r_1^2 - r_2^2)/r_{12}^4$ in the integrand when calculating the matrix elements of H_0, $H_1^{(2)}$, $H_1^{(3)}$ and $H_1^{(4)}$. So a new type of integrals $G(M,N;\alpha,\beta)$ must be introduced, defined by

$$\int \frac{dv_1}{4\pi} \int \frac{dv_2}{4\pi} \frac{r_1^2 - r_2^2}{r_{12}^4} r_1^{M-3} r_2^{N-3} e^{-ar_1} e^{-br_2} = - G(M,N;a,b) + G(N,M;b,a) \tag{A11}$$

where

$$G(M,N;\alpha,\beta) = \int_0^\infty dr\, e^{-\alpha r} \int_r^\infty ds\, e^{-\beta s} s^{N-1}(s^2 - r^2)^{-1}$$

$$= \frac{1}{2} \frac{(M+N-3)!}{\alpha^{M+N-2}} \int_0^1 \frac{du}{u} \frac{(1-u)^{M-1}(1+u)^{N-1}}{(1-u+\beta/\alpha(1+u))^{M+N-2}} \tag{A12}$$

G-integrals are only calculated for $M+N \geqq 3$, they are logarithmically divergent at the lower limit ($r = s$ or $u = 0$). Writing $(1+u)^{N-1} = u(1+u)^{N-2} + (1+u)^{N-2}$ we obtain, after one partial integration:

$$G(M,N;\alpha,\beta) = \frac{1}{2} \frac{(M+N-3)!}{\alpha^{M+N-2}} \int_0^1 \frac{dx}{1+x} \frac{x^{M-1}}{(x+\beta/\alpha)^{M+N-2}} + \mathrm{div}(M,N)$$

$$+ \frac{1}{4}[-(M-1)FL(M-1,N-1;\alpha,\beta) + (N-2)FL(M,N-2;\alpha,\beta)$$

$$- (\beta-\alpha)FL(M,N-1)] \tag{A13}$$

The first integral is convergent and is evaluated by the numerical method of Schwartz,[37] the FL-integrals are tabulated and the divergence is contained in the surface term

$$\mathrm{div}(M,N) = - \frac{1}{2} \frac{(M+N-3)!}{\alpha^{M+N-2}} \lim_{u\to 0} \ln u \frac{(1-n)^{M-1}(1+u)^{N-2}}{(1-u+\beta/\alpha(1+u))^{M+N-2}}$$

$$= - \frac{1}{2} \frac{(M+N-3)!}{(\alpha+\beta)^{M+N-2}} \lim_{u\to 0} \ln u$$

Thus the logarithmic divergences will cancel between the two G-integrals in (A11) if u goes to zero at the same rate in the divergent parts div(M,N)

of the two G-integrals, i.e., if the principal value of the integral on the left-hand side in (A11) is taken at $r_1 = r_2$. Looking at the expression (B0) for a typical matrix element it is seen that the principal value should in fact be taken, writing out (B0) without commuting the operator $1 - P_{12}$ through H one gets two direct and two exchange parts. These occur with the same integral signs and are equal except that r_1 and r_2 are interchanged, thus if we put $u = \epsilon_1$ in one of the G-integrals in (A11) and $u = \epsilon_2$ in the other, at the lower limit, we get a term proportional to $\ln(\epsilon_1/\epsilon_2)$ but then from the other integrals with exchanged variables we get another term proportional to $\ln(\epsilon_2/\epsilon_1)$; so we are justified in taking the principal value. Formula (A13) cannot be used for $N = 1$, but a similar formula, valid for $N = 1$ (but not for $M = 1$) can be obtained by using $(1-u)^{N-1} = - u(1-u)^{N-2} + (1-u)^{N-2}$ in (A12) and doing the partial integration. The G-integrals are only evaluated by these formulas along $M+N = \text{const}$, a backwards recursion formula similar to (A7) is used for $M+N < \text{const}$. There is a formula similar to (A11) for the case when there is a factor $\cos \theta_{12}$ in the integrand on the left-hand side of (A11), this formula contains four G-integrals and two A-integrals, again the divergences cancel among the G-integrals. In all cases where G-integrals are required, the divergences cancel for the exchange and direct parts separately, except for the matrix element of $1/r_{12}$ in H_0 with functions with $1/r_{12}$ on both sides, when the divergences cancel between the direct and exchange integrals. If the functions $\psi_1^{(i)}$ had been symmetric (singlet intermediate states) this cancellation would not have taken place.

Finally, to evaluate the matrix elements of $H_1^{(3)}$ and $H_1^{(4)}$ between standard terms and functions with $1/r_{12}$ we have to define yet another class of divergent integrals:

$$H(M,N;\alpha,\beta) = \int_0^\infty dr\, e^{-\alpha r} \int_r^\infty ds\, e^{-\beta s}\, s^{N-1}(s^2 - r^2)^{-2}$$

which are calculated along $M+N = \text{const}$ after which a backwards recursion formula similar to (A7) is used. These integrals are evaluated by doing the same tricks as for the G-integrals, but two partial integrations are required. The surface terms now give a pole-type singularity as well as a finite contribution. After some algebra we find

$$H(M,N;\alpha,\beta) = -\frac{1}{2}\frac{(M+N-5)!}{\alpha^{M+N-4}}\left[\int_0^1 \frac{dx}{(1+x)^2}\frac{x^{M-2}}{(x+\beta/\alpha)^{M+N-4}} + \mathrm{Div}(M,N;\alpha,\beta)\right]$$

$$+ \left(\frac{1}{2}N-1\right)G(M-1,N-1;\alpha,\beta) - \frac{1}{2}\beta G(M-1,N;\alpha,\beta)$$

where the first integral is done numerically and the surface term is

$$\mathrm{Div}(M,N;\alpha,\beta) = \frac{1}{4}\lim_{u\to 0}\frac{1}{u}\frac{(1-u)^{M-1}(1+u)^{N-1}}{(1-u+\beta/\alpha(1+u))^{M+N-4}}$$

$$= \frac{1}{4}\frac{1}{(1+\beta/\alpha)^{M+N-4}}\left[\lim_{u\to 0}\frac{1}{u} + N - M + \frac{\alpha-\beta}{\alpha+\beta}(M+N-4)\right] \quad \text{(A14)}$$

By looking at the actual combination of integrals involved in the matrix elements, one finds that the logarithmic divergences included in the G-integrals cancels separately for the direct and exchange integrals whenever H-integrals are used and that the pole divergences in (A14) cancels between exchange and direct parts. The finite part of (A14) is important and should of course be included. The H-integrals are only evaluated for $M \geqq 2$, $N \geqq 2$ and $M+N \geqq 5$.

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

$$M_{k'k} = \langle \frac{1 - P_{12}}{4\pi\sqrt{2}} T_1^{(1)}(\vec{r}_1) u_{\ell' m' n'}(1,2) | H | \frac{1 - P_{12}}{4\pi\sqrt{2}} T_1^{(1)}(\vec{r}_1) u_{\ell m n}(1,2) \rangle \quad \text{(B0)}$$

where $u_{\ell mn}(1,2) = e^{-\frac{\kappa\sigma}{2}r_1} e^{-\frac{\kappa}{2}r_2} r_1^m r_2^n r_{12}^\ell$ and the ordering $(\ell',m',n') \longleftrightarrow k'$; $(\ell,m,n) \longleftrightarrow k$ is implied. H is any of the eight operators, every one of these is symmetric in the coordinates of the two electrons, $H = H(1,2) = H(2,1)$, so that

$$M_{k'k} = \int \frac{dv_1}{4\pi} \int \frac{dv_2}{4\pi} [T_1^{(1)*}(\vec{r}_1) u_{\ell' m' n'}(1,2) - T_1^{(1)*}(\vec{r}_2) u_{\ell' m' n'}(2,1)] \times H\, T_1^{(1)}(\vec{r}_1) u_{\ell m n}(1,2)$$

Whenever we have more than one differential operator (∇_1 or ∇_2), it is preferable to let all operators act to 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 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):

$$
\begin{aligned}
H_0 T_1^{(1)}(\vec{r}_1) u_{\ell mn}(1,2) = \{ & T_1^{(1)}(\vec{r}_1)[\tfrac{1}{8}\kappa^2(\sigma^2+1) + \frac{1}{r_1}(\tfrac{1}{4}\kappa\sigma(2m+4+\ell) - Z) \\
& + \frac{1}{r_2}(\tfrac{1}{4}\kappa(2n+2+\ell) - Z) - \frac{1}{r_1^2}\tfrac{1}{2}m(m+3+\ell) \\
& - \frac{1}{r_2^2}\tfrac{1}{2}n(n+1+\ell) - \frac{1}{r_{12}^2}\tfrac{1}{2}\ell(2\ell+4+m+n) + \frac{1}{r_{12}} \\
& + \frac{r_1}{r_{12}^2}\tfrac{1}{4}\kappa\sigma\ell + \frac{r_2}{r_{12}^2}\tfrac{1}{4}\kappa\ell + \frac{r_2^2}{r_1^2 r_{12}^2}\tfrac{1}{2}m\ell \\
& + \frac{r_1^2}{r_2^2 r_{12}^2}\tfrac{1}{2}n\ell - \frac{r_2^2}{r_1 r_{12}^2}\tfrac{1}{4}\kappa\sigma\ell - \frac{r_1^2}{r_2 r_{12}^2}\tfrac{1}{4}\kappa\ell] \\
& + T_1^{(1)}(\vec{r}_2)\frac{\ell}{r_{12}^2}\} u_{\ell mn}(1,2) \qquad \text{(B1)} \\
\equiv \{ & T_1^{(1)}(\vec{r}_1)[\sum_{i=1}^{13} c_i(\ell,m,n;\kappa\sigma,\kappa) r_1^{p_i} r_2^{q_i} r_{12}^{s_i}] \\
& + T_1^{(1)}(\vec{r}_2)\frac{\ell}{r_{12}^2}\} u_{\ell mn}(1,2)
\end{aligned}
$$

Introducing $L = \ell+\ell'$, $MD = m+m'$, $ND = n+n'$, $ME = m+n'$ and $NE = n+m'$ one gets the following formula for the matrix elements:

$$
\begin{aligned}
(M_0)_{k'k} = \tfrac{1}{3}\{ & \sum_{i=1}^{13} c_i(\ell,m,n;\kappa\sigma,\kappa)[ADI(L+2+s_i, MD+4+p_i, ND+2+q_i) \\
& - BEX(L+2+s_i, ME+3+p_i, NE+3+q_i)] \\
& + \ell[BDI(L, MD+4, ND+2) - AEX(L, ME+3, NE+3)]\}
\end{aligned}
$$

It is convenient to write out $H_1^{(i)} T_1^{(1)}(\vec{r}_1) u_{\ell mn}(1,2)$ 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 the three spin-dependent operators act on ψ_o. 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 $\alpha(1)\alpha(2)$.

$$H_1^{(1)}\alpha(1)\alpha(2)T_1^{(1)}(\vec{r}_1)u_{\ell mn}(1,2) = Z\{\alpha(1)\alpha(2)[\frac{1}{r_1^3} + \ell\frac{(\vec{r}_1 \times \vec{r}_2)_o}{i\, r_{12}^2}$$

$$\times (\frac{1}{r_2^3} - \frac{1}{r_1^3})] - \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))\ell\frac{(\vec{r}_1 \times \vec{r}_2)_{+1}}{i\, r_{12}^2}$$

$$\times (\frac{1}{r_2^3} - \frac{1}{r_1^3})\}\, T_1^{(1)}(\vec{r}_1)u_{\ell mn}(1,2) \qquad \text{(B2)}$$

where vectors have been resolved in spherical components:

$$(v)_\pm = \mp(v_x \pm iv_y)/\sqrt{2} \qquad \text{and} \qquad v_o = v_z$$

$$(\vec{r}_1 \times \vec{r}_2)_\lambda = -\, i\sqrt{2}\, T_\lambda^{(1)}(\vec{r}_1 \times \vec{r}_2) = -\, i\sqrt{2}\sum_\mu C(111;\lambda\mu)T_\mu^{(1)}(\vec{r}_1)T_{\lambda-\mu}^{(1)}(\vec{r}_2)$$

$$(\lambda = +1,0,-1)$$

by the usual law for combining spherical tensors; $C(\ell_1\ell_2\ell;m_1m_2)$ are C-G coefficients. The second term in (B2) 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

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

$$= \frac{1}{2}(T_1^{(1)}(\vec{r}_1)(\vec{r}_1\cdot\vec{r}_2) - T_1^{(1)}(\vec{r}_2)r_1^2)$$

which is proportional to $[\vec{r}_1 \times (\vec{r}_1 \times \vec{r}_2)]_{+1}$. So the P-part of (B2) is:

$$Z\alpha(1)\alpha(2)[\frac{1}{r_1^3}T_1^{(1)}(\vec{r}_1) + \frac{\ell}{2r_{12}^2}(\frac{1}{r_2^3} - \frac{1}{r_1^3})(T_1^{(1)}(\vec{r}_1)(\vec{r}_1\cdot\vec{r}_2) - T_1^{(1)}(\vec{r}_2)r_1^2)]$$

$$\times\, u_{\ell mn}(1,2) \qquad \text{(B3)}$$

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:

$$(M_1^{(1)})_{k'k} = \frac{Z}{3}[\mathrm{ADI}(L+2,MD+1,ND+2) - \frac{1}{L}(\ell \mathrm{BEX}(L+2,ME+3,NE) + \ell' \mathrm{BEX}(L+2,ME,NE+3))]$$

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

$$\text{P-part of } H_1^{(2)}\alpha(1)\alpha(2)T_1^{(1)}(\vec{r}_1)u_{\ell mn}(1,2) = \alpha(1)\alpha(2)(\frac{-3}{r_{12}^3})[T_1^{(1)}(\vec{r}_1)$$

$$- T_1^{(1)}(\vec{r}_2) + (- \frac{\kappa\sigma}{2}\frac{1}{r_1} + \frac{m}{r_1^2} + \frac{\kappa}{2}\frac{1}{r_2} - \frac{n}{r_2^2})(T_1^{(1)}(\vec{r}_1)(\vec{r}_1\cdot\vec{r}_2)$$

$$- T_1^{(1)}(\vec{r}_2)r_1^2)]u_{\ell mn}(1,2) \qquad \text{(B4)}$$

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

$$\vec{r}_1\cdot(\vec{r}_1 - \vec{r}_2) = \frac{1}{2}(r_1^2 - r_2^2 + r_{12}^2) \quad \text{and} \quad \vec{r}_2\cdot(\vec{r}_1 - \vec{r}_2) = \frac{1}{2}(r_1^2 - r_2^2 - r_{12}^2)$$

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

$$\int \frac{d\Omega_1}{4\pi}\int \frac{d\Omega_2}{4\pi}\frac{\sin^2\theta_{12}}{r_{12}^2} = \frac{r_1^2 + r_2^2}{4r_1^2r_2^2} - \frac{(r_1^2 - r_2^2)^2}{8r_1^3r_2^3}\ln\frac{r_1 + r_2}{|r_1 - r_2|}$$

is used, so that FL-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:

$$S_0^{(2)}\alpha(1)\alpha(2) = \frac{1}{\sqrt{6}}(2\sigma_{1z}\sigma_{2z} - \sigma_{1x}\sigma_{2x} - \sigma_{1y}\sigma_{2y})\alpha(1)\alpha(2) = \sqrt{2/3}\,\alpha(1)\alpha(2)$$

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

$$\text{P-part of } T_0^{(2)}(\vec{r}_{12})T_1^{(1)}(\vec{r}_1) = \text{P-part of } \frac{1}{\sqrt{6}}(2z_{12}^2 - x_{12}^2 - y_{12}^2)T_1^{(1)}(\vec{r}_1)$$

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

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

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

after some C-G algebra. One had to express $T_\mu^{(2)}(\vec{r}_{12})$ in terms of $T_\lambda^{(\ell)}(\vec{r}_1)$ and $T_\lambda^{(\ell)}(\vec{r}_2)$; one can use a formula due to Rose[38] or work the relations out by inspection. We quote one example:

$$T_0^{(2)}(\vec{r}_{12}) = T_0^{(2)}(\vec{r}_1) + T_0^{(2)}(\vec{r}_2) - 2\sqrt{2/3}\,T_0^{(1)}(\vec{r}_1)T_0^{(1)}(\vec{r}_2)$$
$$- \sqrt{2/3}\,[T_{-1}^{(1)}(\vec{r}_1)T_1^{(1)}(\vec{r}_2) + T_1^{(1)}(\vec{r}_1)T_{-1}^{(1)}(\vec{r}_2)]$$

The result is:

$$\text{P-part of } H_1^{(3)}\alpha(1)\alpha(2)T_1^{(1)}(\vec{r}_1)u_{\ell mn}(1,2) = \frac{1}{5}\frac{1}{r_{12}^5}\alpha(1)\alpha(2)[3T_1^{(1)}(\vec{r}_{12})(\vec{r}_{12}\cdot\vec{r}_1)$$
$$- T_1^{(1)}(r_1)r_{12}^2]u_{\ell mn}(1,2) \qquad \text{(B5)}$$

For the matrix elements one gets:

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

$$- [\frac{(r_1^2 - r_2^2)^2}{2r_{12}^5} - \frac{r_1^2 + r_2^2}{3r_{12}^3} - \frac{1}{6r_{12}}]u_{\ell'm'n'}(2,1)\}u_{\ell mn}(1,2)$$

which can easily be expressed in terms of A, F and FL-integrals, when the cases $L = \ell + \ell' = 0, 1, 2$ 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 $\alpha^2/4$ 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 the constant α^2:

$$H_1^{(4)}T_1^{(1)}(\vec{r}_1)u_{\ell mn}(1,2) = \frac{1}{2}\{T_1^{(1)}(\vec{r}_2)[-\frac{3\kappa}{4}\frac{1}{r_{12}r_2} + \frac{3n}{2}\frac{1}{r_{12}r_2^2} + \frac{2\ell+n/2}{r_{12}^3} - \frac{\kappa}{4}\frac{r_2}{r_{12}^3}$$

$$+ \frac{\kappa}{4}\frac{r_1^2}{r_2r_{12}^3} - \frac{n}{2}\frac{r_1^2}{r_{12}^3r_2^2}] + T_1^{(1)}(\vec{r}_1)[-\frac{\ell(2\ell+2+m+n) + n(m+1)/2}{r_{12}^3}$$

$$+ \frac{\kappa^2\sigma}{8}(\frac{r_1}{r_{12}r_2} + \frac{r_2}{r_{12}r_1}) + \frac{\kappa^2\sigma}{16}(\frac{r_1^3}{r_{12}^3r_2} + \frac{r_2^3}{r_{12}^3r_1} - \frac{2r_1r_2}{r_{12}^3} - \frac{3r_{12}}{r_1r_2}) + \frac{\kappa\sigma}{4}(2\ell+n)\frac{r_1}{r_{12}^3}$$

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

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

$$+ \frac{\kappa}{4}(2\ell+1-m)\frac{1}{r_{12}r_2} - n\,\frac{\kappa\sigma}{4}\,\frac{r_1}{r_{12}r_2^2} - \frac{n}{2}(2\ell+1-m)\frac{1}{r_{12}r_2^2} + \frac{\kappa\sigma}{4}(2\ell-n)\frac{1}{r_{12}r_1}$$

$$- m\,\frac{\kappa}{4}\,\frac{r_2}{r_{12}r_1^2} - \frac{m}{2}(2\ell-n)\frac{1}{r_{12}r_1^2}]\}u_{\ell mn}(1,2) \qquad \text{(B6)}$$

The matrix elements can now be written in terms of A, B, F and FL 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

$$\langle f|\nabla^4 g\rangle = \langle \nabla^2 f|\nabla^2 g\rangle$$

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 (B1) one has:

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

$$\times\, u_{\ell mn}(1,2)$$

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

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

$$
\begin{aligned}
(M_1^{(5)})_{k'k} = -\frac{1}{24}\{ & \sum_{i=1}^{7}\sum_{j=1}^{7} d_i(\ell mn,\kappa\sigma)d_j(\ell'm'n';\kappa\sigma) \\
& \times \mathrm{ADI}(L+2+p_i+p_j, MD+4+q_i+q_j, ND+2+r_i+r_j) + 4\ell\ell' \,\mathrm{ADI}(L-2, MD+2, ND+4) \\
& - 2\ell \sum_{j=1}^{7} d_j(\ell'm'n';\kappa\sigma)\mathrm{BDI}(L+p_j, MD+3+q_j, ND+3+r_j) \\
& - 2\ell' \sum_{i=1}^{7} d_i(\ell mn;\kappa\sigma)\mathrm{BDI}(L+p_i, MD+3+q_i, ND+3+r_i) \\
& + \sum_{i=1}^{7}\sum_{j=1}^{7} h_i(\ell mn;\kappa)h_j(\ell'm'n';\kappa)\mathrm{ADI}(L+2+s_i+s_j, MD+4+t_i+t_j, ND+2+u_i+u_j) \\
& - \sum_{i=1}^{7}\sum_{j=1}^{7} d_i(\ell mn;\kappa\sigma)h_j(\ell'm'n';\kappa)\mathrm{BEX}(L+2+p_i+s_j, ME+3+q_i+u_j, NE+3+r_i+t_j) \\
& + 2\ell \sum_{j=1}^{7} h_j(\ell'm'n';\kappa)\mathrm{AEX}(L+s_j, ME+2+u_j, NE+4+t_j) \\
& - \sum_{i=1}^{7}\sum_{j=1}^{7} h_i(\ell mn;\kappa)d_j(\ell'm'n';\kappa\sigma)\mathrm{BEX}(L+2+p_j+s_i, ME+3+r_j+t_i, NE+3+q_j+u_i) \\
& + 2\ell' \sum_{i=1}^{7} h_i(\ell mn,\kappa)\mathrm{AEX}(L+s_i, ME+4+t_i, NE+2+u_i)\}
\end{aligned}
$$

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 and 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 $ND = 0$ in which case:

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

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

$$H_1^{(7)} T_1^{(1)}(\vec{r}_1) u_{\ell mn}(1,2) = -\{T_1^{(1)}(\vec{r}_2)[-\frac{\kappa}{2}\frac{1}{r_2} + \frac{n}{r_2^2} + \frac{\ell}{r_{12}^2}]$$

$$+ T_1^{(1)}(\vec{r}_1)[-\frac{\ell(\ell+m+n+2)}{r_{12}^2} + \frac{\ell\kappa\sigma}{2}\frac{r_1}{r_{12}^2} + \ell\frac{\kappa}{2}\frac{r_2}{r_{12}^2} + \frac{\kappa^2\sigma}{4}\cos\theta$$

$$- n\frac{\kappa\sigma}{2}\frac{\cos\theta}{r_2} - m\frac{\kappa}{2}\frac{\cos\theta}{r_1} - \ell\frac{\kappa\sigma}{2}\frac{r_2\cos\theta}{r_{12}^2} - \ell\frac{\kappa}{2}\frac{r_1\cos\theta}{r_{12}^2}$$

$$+ mn\frac{\cos\theta}{r_1 r_2} + m\ell\frac{r_2\cos\theta}{r_1 r_{12}^2} + n\ell\frac{r_1\cos\theta}{r_2 r_{12}^2}]\}u_{\ell mn}(1,2) \quad . \qquad \text{(B7)}$$

To evaluate the exchange part of the matrix elements we use $\cos^2\theta = 1 - \sin^2\theta$ and (A4), or we may rewrite (B7) using

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

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 are used also in the cases 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: DETERMINATION OF EIGENVALUES AND EIGENVECTORS

The method employed by Schwartz[11] is used. The matrices $(H_0)_{ij}$ and I_{ij} of H_0 and 1 in some representation are given, and we wish to find E_0 and $\psi_o = (x_1 \ldots x_n)$ such that

$$\sum_{j=1}^{n} [(H_0)_{ij} - E_0 I_{ij}] x_j = 0 \qquad i = 1,2,\ldots,n \quad .$$

The approximative iteration procedure consists in making an initial guess for E_0, put $x_k = 1$ $(1 \leq k \leq n)$ and obtaining $x_1, x_2, \ldots, x_{k-1}, x_{k+1}, \ldots, x_n$ from the inhomogeneous system

$$\sum_{\substack{j=1 \\ j+k}}^{n} [(H_0)_{ij} - E_0 I_{ij}] x_j = - [(H_0)_{ik} - E_0 I_{ik}] \qquad \text{(C1)}$$

$$i = 1,2,\ldots,k-1,k+1,\ldots,n$$

from which a new value for E_0, call it E_0', is gotten from the Rayleigh quotient

$$E_0' = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (H_0)_{ij} \Big/ \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j I_{ij} \qquad \text{(C2)}$$

or $E_0' = \langle \psi_o | H_0 | \psi_o \rangle / \langle \psi_o | \psi_o \rangle$. Then put $E_0 = E_0'$ and continue the alternating iteration (C1), (C2) until $|E_0 - E_0'| < \epsilon$ where ϵ is some small number. In the standard (unmixed) basis the matrices are symmetric and we put $k = 1$ since the first term is the most important when the nonrelativistic wavefunction is expanded in the standard basis, see page 20. This method works well, with rapid convergence if the initial value of E_0 is a very good guess. In Fig. 3a and Fig. 3b E_0' is plotted versus E_0 for the matrices in the standard representation when $\omega = 3$, i.e., for matrices of dimension 20. For each of the two graphs one hundred points were computed. In Fig. 3a three eigenvalues are seen where the line of 45° slope is tangent to the curve. Figure 3b is an enlargement of the curve in Fig. 3a in the neighborhood of the lowest eigenvalue. Unless the initial guess for

E_0 is such that the curve lies below the 45°-line for this value of E_0, the iterations will not converge. The dashed lines in Fig. 3a show what happens after three iterations when the initial guess is too far from the desired eigenvalue. The method is good only as long as one has at least the three or four first digits of the lowest eigenvalue to start with. For $\omega = 2$ and 3 we tried to vary κ and σ and find E_0 for each choice, but after some small changes in κ and σ this procedure converged on some of the higher eigenvalues.

As mentioned in the text (page 21) we used $\epsilon = 10^{-11}$ for $1 \leqq \omega \leqq 5$ and $\epsilon = 10^{-10}$ for $6 \leqq \omega \leqq 8$, and obtained convergence. Then one more iteration was performed to get a slightly different ψ_o, but this sometimes caused the eigenvalue E_0 to change by an amount larger than ϵ, so the convergence was probably accidental. For $6 \leqq \omega \leqq 8$ the eigenvalues $E_0 \approx -2.1331$ were nevertheless converged to at least nine digits. The differences between the two ψ_o's (whose eigenvalues differed by an amount less than ϵ) was of course larger, for $\omega = 8$ the values for x_2 were 0.31938 and 0.31939 respectively, and the last element of the eigenvectors were 9×10^{-8} and 1×10^{-7} for the two ψ_o's.

The eigenvalue problem in the extended bases of Section VII were solved for $\tilde{E}_0$ and $\tilde{\psi}_o$ by the same method, except that k in (C1) was put equal to $\omega+2$, corresponding to the first standard term in the expansions (48), (53), (54), or (55). The convergence was sometimes slow and we had to settle with $\tilde{E}_0$'s converged to fewer digits than E_0 for the same ω. In the case where the matrices $(H_0)_{ij}$ and I_{ij} are unsymmetric (the mixed representation used to calculate $E_2^{(1,6)}$ in Section VII) a slight modification of the algorithm is required. An approximation to the right eigenvector $\tilde{\psi}_o^r$ is obtained from (C1) with $\tilde{E}_0$ replacing E_0, but the left eigenvector $\tilde{\psi}_o^\ell$ is also needed, it is gotten from

$$\sum_{\substack{j=1 \\ j\neq k}}^{n} [(H_0)_{ji} - \tilde{E}_0 I_{ji}]x_j = - [(H_0)_{ki} - \tilde{E}_0 I_{ki}]$$

$$i = 1,2,\ldots,k-1,k+1,\ldots,n$$

i.e., the left eigenvector is the same as the right eigenvector of the transposed matrix. The Rayleigh quotient in this case is

$$\tilde{E}_0' = \langle\tilde{\Psi}_o^{\ell}|H_0|\tilde{\Psi}_o^{r}\rangle/\langle\tilde{\Psi}_o^{\ell}|\tilde{\Psi}_o^{r}\rangle$$

The convergence of $\tilde{E}_0$ for this unsymmetric case was rather slow.

APPENDIX D: SPIN-INDEPENDENT SECOND-ORDER ENERGIES

The spin-independent second-order energies calculated along with the spin-dependent ones in Section VI are listed in Table XI, with the same convention for the number of digits quoted as in Section VI. $E_2^{(4,4)}$ was also calculated with the expansions (54) and (55) of Section VII for $\psi_1^{(4)}$, the results were very close to those of Table XI. For $\omega = 8$ the values -0.0384789(1) and -0.0385239 were obtained, using (54) and (55) respectively.

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):

$$E_2^{true} = \langle \Psi_1 | H_0 - E_0 | \Psi_1 \rangle + 2\langle \Psi_1 | H_1 - E_1 | \Psi_0 \rangle \tag{D1}$$

where the (exact) perturbed function Ψ_1 satisfies

$$(H_0 - E_0)\Psi_1 = -(H_1 - E_1)\Psi_0 \tag{D2}$$

assuming that the unperturbed wavefunction and energy Ψ_0 and E_0 are known exactly. In practice the expression (D1) is calculated by using an approximation ψ_1 to Ψ_1, $\psi_1 = \Psi_1 + \Delta\psi_1$ so that

$$E_2^{calc} = E_2^{true} + \langle \Delta\psi_1 | H_0 - E_0 | \Delta\psi_1 \rangle + 2\langle \Delta\psi_1 | H_0 - E_0 | \Psi_1 \rangle + 2\langle \Delta\psi_1 | H_1 - E_1 | \Psi_0 \rangle \tag{D3}$$

The two last terms of (D3) cancel because of (D2), the second term of (D3) 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 $E_2^{calc} \geq E_2^{true}$ 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.

Table XI

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

ω	$E_2^{(4,4)}$ $(2\alpha^4$ Ry)	$E_2^{(5,5)}$ $(2\alpha^4$ Ry)	$E_2^{(6,6)}$ $(2\alpha^4$ Ry)	$E_2^{(7,7)}$ $(2(\frac{m}{M})^2$ Ry)	$E_2^{(4,5)}$ $(2\alpha^4$ Ry)
1	-0.019941220293	-252.29957845	-89.151341771	-0.067054443539	-0.50960789526
2	-0.028765953478	-349.3225438	-108.81860313	-0.12139468080	0.03804557052
3	-0.03333580832	-442.9295373	-133.13685157	-0.14226638400	-0.10323505458
4	-0.03590682884	-534.4092377	-155.75170849	-0.1608640252	-0.0404388526
5	-0.037393840	-621.79741	-177.7267	-0.18066290	-0.0733325
6	-0.0380736	-708.1	-199.26	-0.191578	-0.05552(1)
7	-0.0383437	-793.0	-220.50	-0.19615	-0.06256(1)
8	-0.0384779	-877.3	-241.56	-0.20010	-0.0559(2)

Table XI (continued)

ω	$E_2^{(4,6)}$ $(2\alpha^4$ Ry)	$E_2^{(4,7)}$ $(2\alpha^2 \frac{m}{M}$ Ry)	$E_2^{(5,6)}$ $(2\alpha^4$ Ry)	$E_2^{(5,7)}$ $(2\alpha^2 \frac{m}{M}$ Ry)	$E_2^{(6,7)}$ $(2\alpha^2 \frac{m}{M}$ Ry)
1	0.297444454540	0.033581361648	149.92960428	1.1798445008	-0.66895688907
2	0.01712544041	0.053384471490	194.06528344	-0.1280635666	-0.02039860831
3	0.09295684687	0.062084852257	241.74706234	0.45410128699	-0.3203447117
4	0.064126857	0.06795106559	287.2351047	0.06881801	-0.134151816
5	0.0821650	0.07238333	331.05116	0.3670018	-0.2873564
6	0.07406	0.0744489	371.4	0.1671	-0.1894
7	0.07796(1)	0.075196	416.6	0.2876(1)	-0.2499
8	0.07491(1)	0.075703	458.7	0.1992(1)	-0.2061

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 delta-functions when acting on ψ_o, thus $\psi_1^{(5)}$ and $\psi_1^{(6)}$ should have terms proportional to $(1 - P_{12})T_1^{(1)}(\vec{r}_1)/r_2$ as in (53). This makes the second-order energies $E_2^{(i,j)} = \langle\psi_1^{(i)}|H_1^{(j)} - E_1^{(j)}|\psi_o\rangle$ $(i,j = 5,6)$ proportional to an integral with $\delta^{(3)}(\vec{r}_2)$ (from $H_1^{(j)}$) and $1/r_2$ (from $\psi_1^{(i)}$) and ψ_o, which is regular, under the integral sign, and this is obviously divergent. When only standard terms are used in the expansions for $\psi_1^{(5)}$ and $\psi_1^{(6)}$, they try to approximate the pole-terms in (53), so the second-order energies should diverge as more standard terms are included in the expansions for $\psi_1^{(5)}$ and $\psi_1^{(6)}$, as in fact they do. 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., the 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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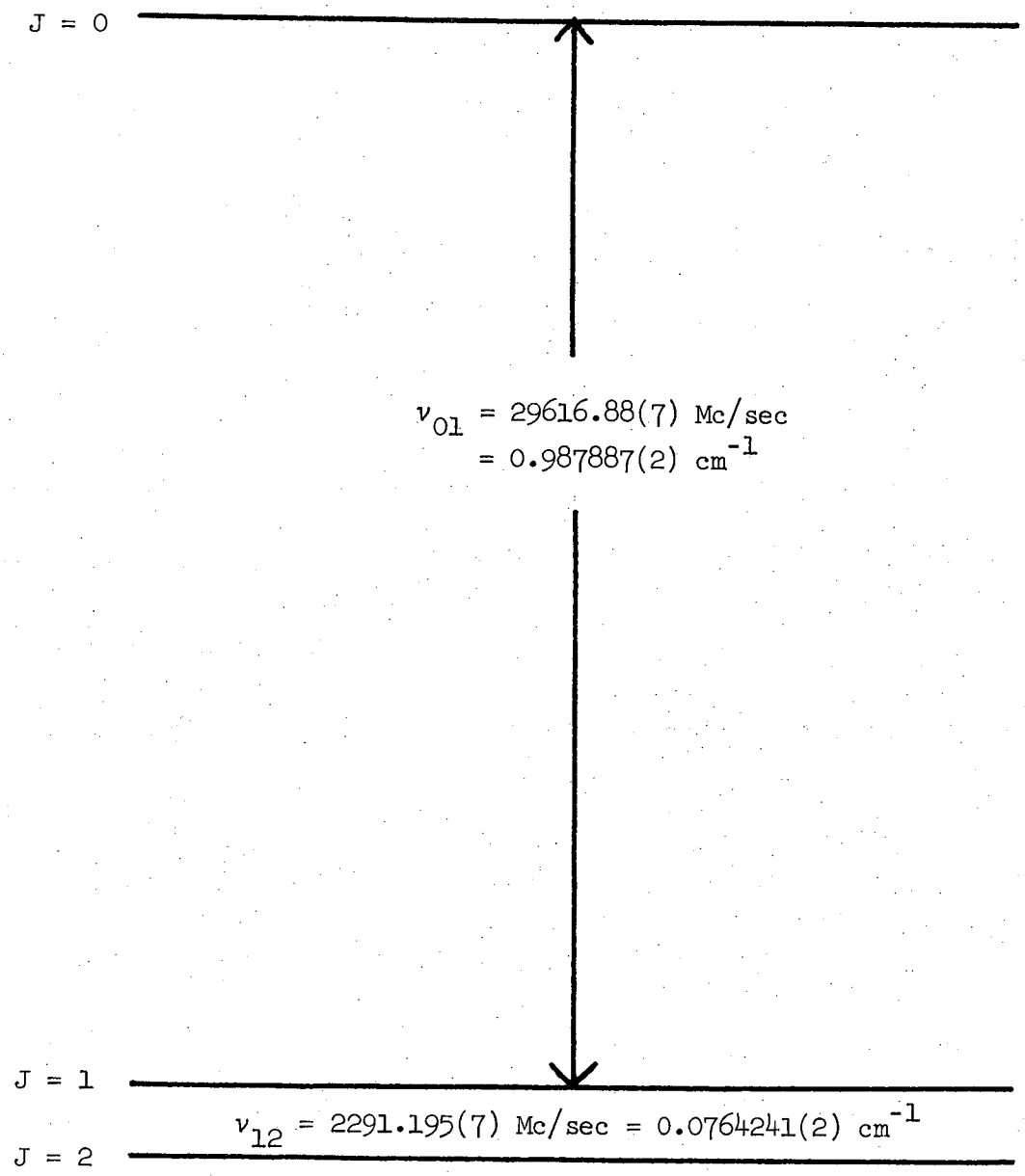

Fig. 1

Fine structure of the 2^3P state of helium.

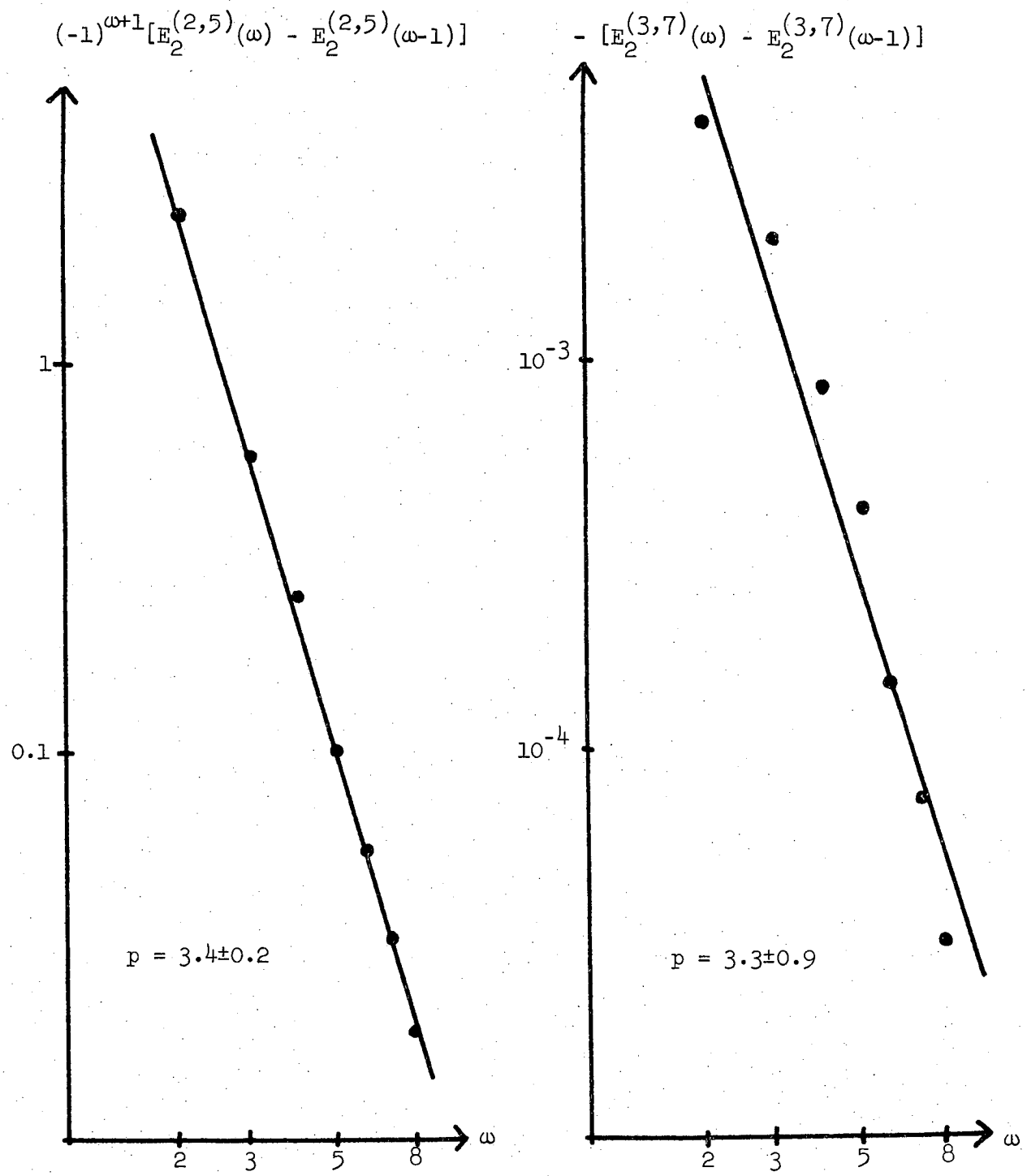

Fig. 2

Successive differences between calculated second-order energies $E_2^{(i,j)}$ versus ω.

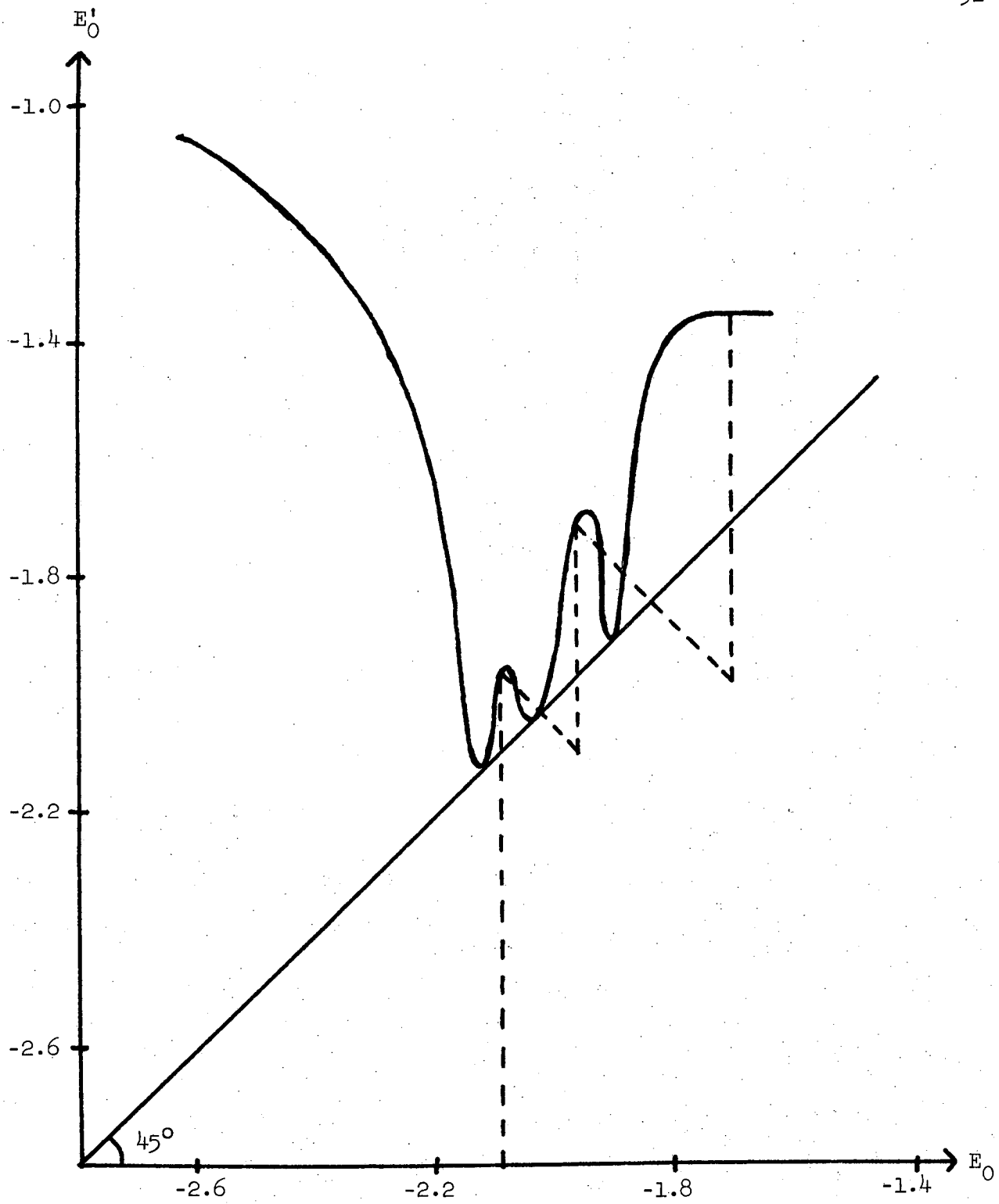

Fig. 3a

E_0' as a function of E_0 for matrices H_0 and I of dimension 20.

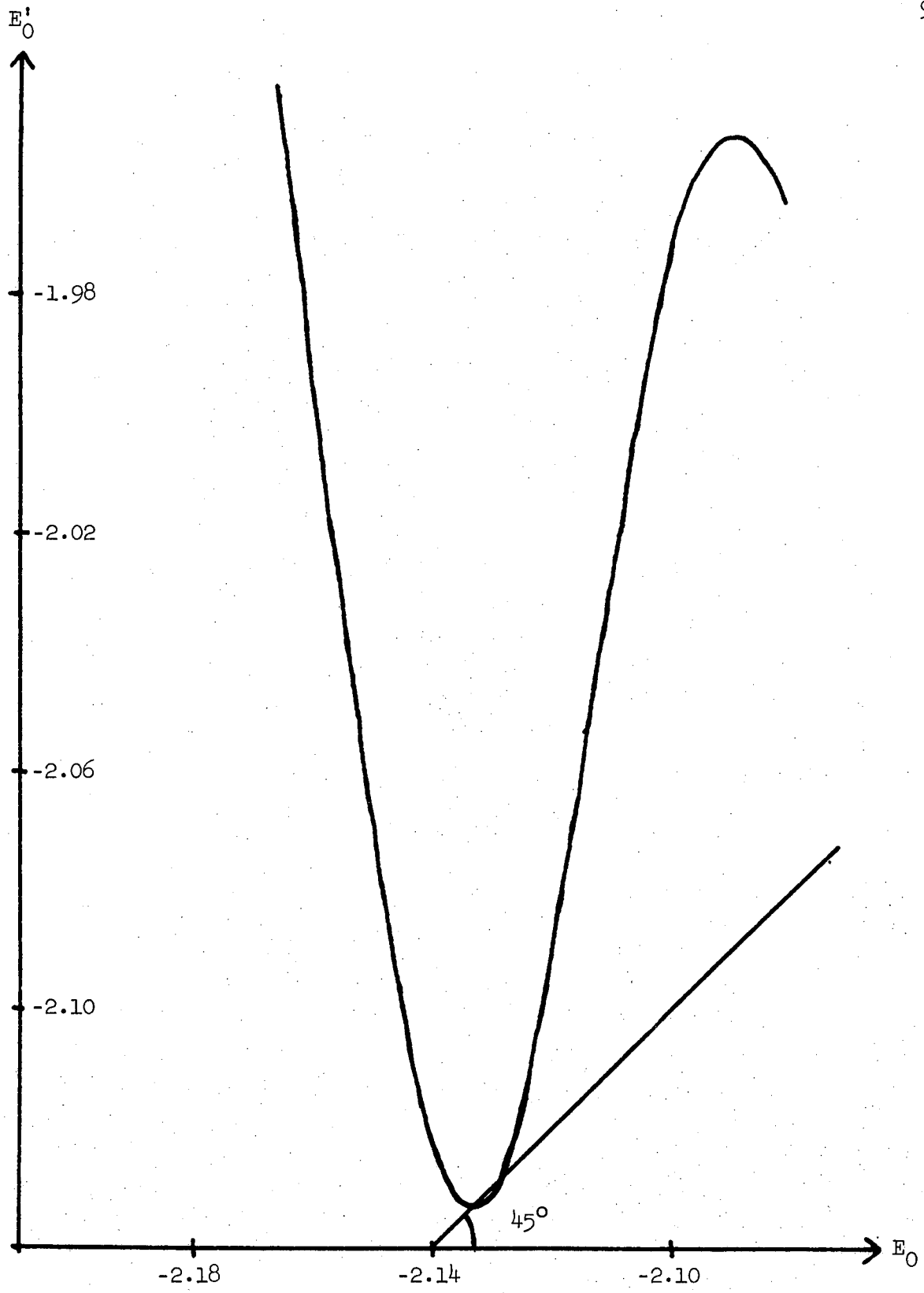

Fig. 3b

E_0' as a function of E_0 for matrices H_0 and I of dimension 20.

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