

It is apparent from the equations for the reduced matrix elements that

$$\hbar\gamma = g\mu_B, \quad (\text{A10})$$

where μ_B is the Bohr magneton and g is a constant usually between $\frac{1}{2}$ and 2.

Note added in proof. The conditions which were placed on Γ and λ in the integral formulation which is given by Eq. (3) are more restrictive than necessary. C. P. Yang and C. V. Heer have shown that an integral solution of

Eq. (2) exists if a part of Γ commutes with H_0 . Then Eq. (2) has the integral solution

$$\rho(t) = \int_0^\infty ds T^+(s) \times \{\lambda + [(V/i\hbar - \frac{1}{2}\Gamma_1)\rho - \rho(V/i\hbar + \frac{1}{2}\Gamma_1)]\}_{(t-s)} T(s),$$

where $T(s) = \exp[-(\frac{1}{2}\Gamma_0 - i\hbar^{-1}H_0)s]$. No restrictions are placed on λ and Γ_1 , and $\Gamma_0 > 0$ is sufficient.

$2^{1,3}P$, $3^{1,3}P$, and $4^{1,3}P$ States of He and the 2^1P State of Li^+

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A method is outlined for calculating nonrelativistic eigenvalues and wave functions for a two-electron P state of odd parity, and for evaluating the mass polarization and all of the relativistic corrections, apart from the radiative terms. Calculations have been made for the low-lying P states of He and the 2^1P state of Li^+ using up to 560 terms in the expansion of the wave function. The nonrelativistic eigenvalues converge to within an accuracy of from 10^{-4} cm^{-1} to 10^{-2} cm^{-1} . The values of the mass polarization and of the relativistic corrections converge more rapidly than this, so that the total theoretical ionization energy is estimated to be correct to within an error of not more than 10^{-2} cm^{-1} , i.e., considerably less than the experimental error, in the case of all of the states considered. The difference between the theoretical and experimental term values is in no case greater than 0.1 cm^{-1} in absolute magnitude, and is presumed to be due to the contributions from the radiative terms, which have not been included in the calculation. The term value obtained for the 2^1P state of Li^+ confirms the identification of the line at 9581.42 \AA in the Li^+ spectrum as belonging to the 2^1S-2^1P transition.

I. INTRODUCTION

IN this paper, we outline a method for determining two-electron atom P -state term values in which the contributions from the mass-polarization and all of the relativistic corrections, apart from the Lamb shift, have been taken into account. Computations have been carried out for the low-lying P states of helium, and the 2^1P state of Li^+ , and in each case the results converge to an accuracy exceeding that of the experimental measurements. The same methods have also been used to compute the fine-structure splitting of the 2^3P and 3^3P levels of helium, the results for which have been published previously.¹

The classical papers of Breit on the angular dependence of a two-electron P -state wave function² and the fine-structure splitting of the helium 2^3P level³ appeared soon after the basic work of Hylleraas on the ground state.^{4,5} Subsequent calculations for the P state were mainly performed with the object of determining the fine structure of the 3P levels, and in contradistinction

to the case of the S state, no complete calculation of the relativistic corrections for a two-electron P state has up till now been made, no doubt in view of their greater complexity. We shall therefore give considerable detail in the following exposition.

At the time when the work to be described below was started, the most accurate calculations for a two-electron P state were those of Araki *et al.*⁶ and of Traub and Foley.⁷ The latter authors were able to obtain a theoretical ionization energy within 15 cm^{-1} of the experimental value for the helium 2^3P state by optimizing the values adopted for the screening constants for the two electrons, and by including 18 terms in the expansion of the wave function. We set out with the aim of computing ionization energies for two-electron P states to an accuracy which would at least match that of the most recent experimental data^{8,9} ($\pm 0.03 \text{ cm}^{-1}$). The method used to determine the nonrelativistic eigenvalues and wave functions is an extension of that developed by one of us for excited S states,¹⁰ the wave function being

¹ B. Schiff, C. L. Pekeris, and H. Lifson, Phys. Rev. **137**, A1672 (1965).

² G. Breit, Phys. Rev. **35**, 569 (1930).

³ G. Breit, Phys. Rev. **36**, 383 (1930).

⁴ E. A. Hylleraas, Z. Physik **48**, 469 (1928).

⁵ E. A. Hylleraas, Z. Physik **54**, 347 (1929).

⁶ G. Araki, K. Mano, and M. Ohta, Progr. Theoret. Phys. (Kyoto) **22**, 469 (1959).

⁷ J. Traub and H. M. Foley, Phys. Rev. **116**, 914 (1959).

⁸ G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).

⁹ G. Herzberg and H. R. Moore, Can. J. Phys. **37**, 1293 (1959).

¹⁰ C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

developed into a series of perimetric coordinates.¹¹ With 220 terms in the expansion of the wave function, the nonrelativistic ionization energy for the 2^3P state of helium was found to converge to within about 0.2 cm^{-1} .¹² Optimizing the values of the screening constants, following Traub and Foley, reduced the inaccuracy to about 0.002 cm^{-1} with the same number of terms, and it was therefore decided to embark on a more extensive program of calculation. Using up to 560 terms in the expansion of the wave function, eigenvalues were obtained for the 2^1P , 2^3P , 3^1P , 3^3P , 4^1P , and 4^3P states of helium and the 2^1P state of Li⁺, the results converging to within an accuracy of 10^{-4} to 10^{-2} cm^{-1} . For each of these states, we have also, for the first time, computed the values of all of the relativistic corrections apart from the radiative terms. These corrections converge more rapidly than the nonrelativistic eigenvalues, and the total theoretical ionization energy is thus subject to an inaccuracy of not more than 10^{-2} cm^{-1} , i.e. less than that of experiment, for all of the states considered. The difference between the theoretical and experimental term values is in no case greater than 0.1 cm^{-1} , and is presumably due to the contributions from the radiative terms. Nonrelativistic eigenvalues and wave functions of the same order of accuracy have recently been obtained for the 2^3P state of helium by Schwartz,¹³ who has used them to compute the fine-structure splitting of this level. With his choice of base functions, Schwartz's nonrelativistic eigenvalues are more accurate than those obtained by the present authors using a given number of terms in the expansion.

The computations on the 2^1P state of Li⁺ were performed in order to check the previously assumed term value for this level, in view of the uncertainty in the position of the 2^1S - 2^1P line in the Li⁺ spectrum. Together with the 2^1S term value computed by one of us,¹⁴ the results confirm the identification of the line at about 9581 \AA as belonging to the 2^1S - 2^1P transition.¹⁵

The methods used for solving the nonrelativistic equation are discussed in Sec. II of this paper, and the evaluation of the mass polarization and relativistic corrections is described in Sec. III. In Sec. IV, the numerical results are tabulated and discussed. The appendices contain an outline of the methods used to reduce some of the sixfold integrals occurring in the calculation, including some explicit formulas for the evaluation of the resulting threefold integrals.

II. THE NONRELATIVISTIC EIGENVALUES

A. The Variational Equations

The nonrelativistic Schrödinger equation for a two-electron atom, assuming an infinitely heavy nucleus,

¹¹ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

¹² C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).

¹³ C. Schwartz, Phys. Rev. **134**, A1181 (1964).

¹⁴ C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

¹⁵ T. G. Toresson and B. Edlén, Arkiv Fysik **23**, 117 (1963).

is

$$\nabla_1^2\psi + \nabla_2^2\psi + 2\left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_3}\right)\psi = 0, \quad (1)$$

where r_1 and r_2 are the distances of the electrons from the nucleus, r_3 is the interelectron distance, Z is the nuclear charge, and ∇_1^2 and ∇_2^2 are the Laplacian operators with respect to the coordinates of the two electrons. Lengths and the energy are expressed in atomic units. The equation may also be written symbolically

$$(\mathcal{H} - E)\psi = 0, \quad (2)$$

where \mathcal{H} is the Hamiltonian operator, and we solve this equation by using the equivalent variational form

$$\delta \int \psi(\mathcal{H} - E)\psi d\tau = 0. \quad (3)$$

The integration is taken over the six-dimensional space of the two electrons, and we will describe the set of coordinates used in some detail, as they will also be employed in computing the relativistic corrections (see Appendix A).

The most suitable set of coordinates to describe our system is one in which the shape of the triangle formed by the nucleus and the two electrons is specified by the variables r_1 , r_2 , and r_3 defined above, while the orientation of this triangle in space is given in terms of three Eulerian angles. Since the Hamiltonian is invariant with respect to rotation about any axis through the nucleus, the dependence of the wave function on the Eulerian angles may be determined uniquely. Any integral similar to that occurring in Eq. (3) may therefore easily be reduced to a threefold integral over the variables r_1 , r_2 , and r_3 .

The angular dependence of a two-electron P -state wave function has been considered in detail by Breit² and by Eriksson,¹⁶ and we shall use Breit's form for the wave function. Following Hylleraas,⁴ Breit uses the Eulerian angles θ' , ϕ' and ϕ , which are simply related to the spherical polar coordinates (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) of the two electrons. The angles θ' and ϕ' are equal respectively to θ_1 and ϕ_1 , and hence describe the position of the line joining electron 1 to the nucleus, while ϕ is the angle between the azimuthal plane through this line and the \mathbf{r}_1 , \mathbf{r}_2 plane, as shown in Fig. 1. Hylleraas also introduces the angle θ included between \mathbf{r}_1 and \mathbf{r}_2 , and gives relations between the two sets of angles $(\theta_1, \phi_1, \theta_2, \phi_2)$ and $(\theta, \theta', \phi', \phi)$. Recently, Bhatia and Temkin¹⁷ have given a comprehensive treatment of the angular dependence of a two-electron state of arbitrary angular momentum, using a more symmetric choice of

¹⁶ A. Eriksson, Nova Acta Regiae Soc. Sci. Upsaliensis **11**, No. 9 (1940).

¹⁷ A. K. Bhatia and A. Temkin, Rev. Mod. Phys. **36**, 1050 (1964).

tion procedure. Double precision arithmetic was used throughout the calculation, and the eigenvalue usually converged to within almost full double precision accuracy in four or five iterations, provided that the initial trial values of E were chosen sufficiently carefully. In the case of the D scheme, the elements of the matrix of coefficients S_{ij} are linear in the energy E . We were thus able to use the Rayleigh quotient procedure for the iteration once the eigenvalue had been located approximately, with a consequent reduction in the number of iterations needed.

III. THE MASS POLARIZATION AND RELATIVISTIC CORRECTIONS

A. Mass Polarization Correction

Our computations so far have been based on the non-relativistic Schrödinger equation (1), in which we have assumed the mass of the nucleus to be infinite. The eigenvalue has therefore first to be corrected to take into account the finite mass of the nucleus and the consequent nuclear motion. An elementary correction is to use a Rydberg constant R_M appropriate for the atom in question,

$$R_M = \frac{M}{m+M} R_\infty \sim \left(1 - \frac{m}{M}\right) R_\infty,$$

where m and M are the masses of an electron and of the nucleus respectively. A second correction, the so-called mass polarization correction, is given by,¹⁸

$$\epsilon_M = -\frac{m}{M} \int \psi (\nabla_1 \cdot \nabla_2) \psi d\tau = \frac{m}{M} \int \nabla_1 \psi \cdot \nabla_2 \psi d\tau, \quad (11)$$

where ∇ is the gradient operator. Using their symmetric Eulerian angles, Bhatia and Temkin have recently¹⁹ extended their treatment¹⁷ of the nonrelativistic Schrödinger equation (1) for two-electron states of arbitrary angular momentum by including the mass polarization term $2(m/M)(\nabla_1 \cdot \nabla_2)\psi$ directly in this equation from the beginning. We shall, however, evaluate ϵ_M from Eq. (11) and add it to the eigenvalue of Eq. (1).

B. The Relativistic Corrections

As mentioned in the introduction, the eigenvalue of Eq. (1) has also to be corrected in order to take relativistic effects into account. The corrections to order α^2 have been listed by Bethe and Salpeter.²⁰ These corrections take the form of the sum of the expectation values of a number of operators, evaluated over the state in question. In atomic units, the operators may be

¹⁸ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 166.

¹⁹ A. K. Bhatia and A. Temkin, *Phys. Rev.* **137**, A1335 (1965).

²⁰ See Ref. 18, p. 181.

written as follows:

$$\begin{aligned} H_1 &= -\frac{1}{8}\alpha^2(p_1^4 + p_2^4), \\ H_2 &= -\frac{\alpha^2}{2} \left[\frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r_3} + \frac{\mathbf{r}_3 \cdot (\mathbf{r}_3 \cdot \mathbf{p}_1) \mathbf{p}_2}{r_3^3} \right], \\ H_3 &= \frac{\alpha^2}{2} \left[\left\{ \frac{Z\mathbf{r}_1 \times \mathbf{p}_1}{r_1^3} - \frac{\mathbf{r}_3 \times (2\mathbf{p}_2 - \mathbf{p}_1)}{r_3^3} \right\} \cdot \mathbf{s}_1 \right. \\ &\quad \left. + \left\{ \frac{Z\mathbf{r}_2 \times \mathbf{p}_2}{r_2^3} + \frac{\mathbf{r}_3 \times (2\mathbf{p}_1 - \mathbf{p}_2)}{r_3^3} \right\} \cdot \mathbf{s}_2 \right], \quad (12) \\ H_4 &= \frac{i\alpha^2}{4} \left[\mathbf{p}_1 \cdot \left\{ \frac{Z\mathbf{r}_1}{r_1^3} - \frac{\mathbf{r}_3}{r_3^3} \right\} + \mathbf{p}_2 \cdot \left\{ \frac{Z\mathbf{r}_2}{r_2^3} - \frac{\mathbf{r}_3}{r_3^3} \right\} \right], \\ H_5 &= \alpha^2 \left[-\frac{8\pi}{3} (\mathbf{s}_1 \cdot \mathbf{s}_2) \delta(\mathbf{r}_3) \right. \\ &\quad \left. + \frac{1}{r_3^3} \left\{ \mathbf{s}_1 \cdot \mathbf{s}_2 - \frac{3(\mathbf{s}_1 \cdot \mathbf{r}_3)(\mathbf{s}_2 \cdot \mathbf{r}_3)}{r_3^2} \right\} \right]. \end{aligned}$$

\mathbf{p}_1 and \mathbf{p}_2 are the momenta of the two electrons, $\delta(\mathbf{r})$ is the three-dimensional delta function, \mathbf{s}_1 and \mathbf{s}_2 are the Pauli spin operators for the two electrons, and $\mathbf{r}_3 = \mathbf{r}_2 - \mathbf{r}_1$. A simple derivation of each of these terms, together with an explanation of their physical significance, has also been given by Stewart.²¹

The total contribution of the relativistic effects to the term value is given by the sum of the expectation values of the operators H_1 to H_5 . It is customary to express the energies in terms of the ionization potential J . Since, to order α^2 , the relativistic effects shift the level of a single-electron atom or ion by an amount $-(\alpha^2 Z^4/8)$, the relativistic contribution to order α^2 to the ionization potential of a two-electron atom or ion is

$$E_J = -\frac{1}{8}\alpha^2 Z^4 - \langle H_1 + H_2 + H_3 + H_4 + H_5 \rangle. \quad (13)$$

As the operators H_3 and H_5 are spin-dependent, their expectation values will depend on the value of the total angular momentum quantum number J . We have evaluated E_J for $J=1$ in the case of a 3P state in view of the term value for the 2^3P_1 state measured by Herzberg.⁸ The values of E_J for $J=0$ and $J=2$ may then be easily deduced using our previously published¹ results for the fine-structure splittings (in the case of the 2^3P , 3^3P and 4^3P states of helium, the $J=2$ levels lie deepest). As shown in Appendix A, the expectation values of the spin-dependent operators may be written in the form

$$\langle H_3 + H_5 \rangle = 2\pi\alpha^2 \langle \delta(\mathbf{r}_3) \rangle \quad (14)$$

for a 1P state, and

$$\langle H_3 + H_5 \rangle = -C + (5D/3) \quad (15)$$

²¹ A. L. Stewart, *Advan. Phys.* **12**, 299 (1963).

for a 3P_1 state, where the integrals C and D are defined in the Appendix.

Using the fact that

$$\langle H_1 \rangle = -\frac{1}{4}\alpha^2 \langle p_1^4 \rangle \quad (16)$$

and²²

$$\langle H_4 \rangle = \pi\alpha^2 [Z\langle \delta(\mathbf{r}_1) \rangle - \langle \delta(\mathbf{r}_3) \rangle], \quad (17)$$

and writing

$$\langle H_2 \rangle = E_2 = \alpha^2 X, \quad (18)$$

we have

$$E_J = \alpha^2 \left[-\frac{1}{8}Z^4 + \frac{1}{4}\langle p_1^4 \rangle - X - \pi Z\langle \delta(\mathbf{r}_1) \rangle - \pi\langle \delta(\mathbf{r}_3) \rangle \right] \quad (19)$$

for a 1P state, and

$$E_J = \alpha^2 \left[-\frac{1}{8}Z^4 + \frac{1}{4}\langle p_1^4 \rangle - X - \pi Z\langle \delta(\mathbf{r}_1) \rangle \right] + C - (5D/3) \quad (20)$$

for a 3P_1 state.

Finally, if we denote by ν the nonrelativistic ionization energy, then the calculated ionization potential will be

$$J_{\text{th}} = \nu - \epsilon_M + E_J. \quad (21)$$

C. Evaluation of the Integrals

It will be seen that the mass polarization and relativistic corrections are obtained by evaluating integrals of the form $\int (O_1\psi)(O_2\psi)d\tau$, where O_1 and O_2 may be scalar, vector, or tensor operators compounded out of the gradient operators ∇_1 and ∇_2 and the vectors \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 , \mathbf{s}_1 , and \mathbf{s}_2 , and the integration is over the space of the two electrons. After summing over the spin coordinates, we are left with a sixfold integral to evaluate. This integral may be reduced to a threefold one by integrating analytically over the angular variables θ' , ϕ' , and ϕ , the methods used differing slightly for various operators. The principal steps in each case are outlined in Appendix A, in which the resulting integrals over the remaining variables r_1 , r_2 , and r_3 are also listed. The resulting threefold integrals consist of sums of terms of the form

$$\int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} \int_{r_3=|r_1-r_2|}^{r_1+r_2} r_1^f r_2^g r_3^h Y(r_1, r_2, r_3) \times Z(r_1, r_2, r_3) e^{-\lambda r_1 - \mu r_2} dr_1 dr_2 dr_3, \quad (22)$$

where

$$Y(r_1, r_2, r_3) = \sum_i B_i r_1^{p_i} r_2^{q_i} r_3^{t_i} \times \frac{\partial^{l_i+m_i+n_i}}{\partial r_1^{l_i} \partial r_2^{m_i} \partial r_3^{n_i}} P(r_1, r_2, r_3) \quad (23)$$

and

$$Z(r_1, r_2, r_3) = \sum_j C_j r_1^{v_j} r_2^{u_j} r_3^{w_j} \times \frac{\partial^{l_j+m_j+n_j}}{\partial r_1^{l_j} \partial r_2^{m_j} \partial r_3^{n_j}} Q(r_1, r_2, r_3). \quad (24)$$

The B_i and C_j are constants. $P(r_1, r_2, r_3)$ is the function $M(r_1, r_2, r_3)$, and $Q(r_1, r_2, r_3)$ is either the function $M(r_1, r_2, r_3)$, in which case $\lambda = 2\xi$ and $\mu = 2\eta$, or the function $\tilde{M}(r_1, r_2, r_3)$, in which case $\lambda = \mu = \xi + \eta$. Both $Y(r_1, r_2, r_3)$ and $Z(r_1, r_2, r_3)$ are thus linear combinations of $M(r_1, r_2, r_3)$ and its derivatives multiplied by various powers of r_1 , r_2 , and r_3 , or a similar function of $\tilde{M}(r_1, r_2, r_3)$. The extra factor $r_1^f r_2^g r_3^h$ could, of course, be incorporated into one of the functions $Y(r_1, r_2, r_3)$ or $Z(r_1, r_2, r_3)$. The integral has been defined in the particular form (22) in order to correspond to the form in which it is evaluated by the computer program.

Integrals of the more general form $\int (O_1\psi_A)(O_2\psi_B)d\tau$, where ψ_A and ψ_B refer to two different states of a two-electron atom, or ion, may also be reduced to the form (22) provided that the wave functions ψ_A and ψ_B are written in a form analogous to that assumed for the P -state functions in the present work, i.e., they consist of terms of the form $e^{-\xi r_1 - \eta r_2} f(\theta', \phi', \phi) \sum D(l, m, n) r_1^l r_2^m r_3^n$. In this case, the functions $P(r_1, r_2, r_3)$ and $Q(r_1, r_2, r_3)$ will be derived from the wave functions for states A and B respectively, and λ and μ will be combinations of the corresponding coefficients ξ_A , η_A , ξ_B , η_B occurring in the exponential factors. The computational scheme was therefore designed from the beginning to deal with the more general case, and was also used to obtain our previously reported results for the transition probabilities between S and P states in helium²³ and for computing the fine-structure splittings of the 2^3P and 3^3P levels in this atom.¹ The main contributions to the fine-structure splittings had previously^{1,2} been calculated by transforming integrals of the type (22) from the (r_1, r_2, r_3) scheme to the variables u, v, w defined in equations (7) and (8) above. However, in view of the complicated form of the integral to be evaluated in the present computation, especially for the expectation value of p_1^4 , it was decided to perform the integration directly in terms of the variables r_1 , r_2 , and r_3 . If we write the functions $P(r_1, r_2, r_3)$ and $Q(r_1, r_2, r_3)$ as triple series in r_1 , r_2 , and r_3 , the integral (22) may be written in the form $\sum C(a, b, c) \times I(a, b, c)$, where

$$I(a, b, c) = \int_{r_1=0}^{\infty} \int_{r_2=0}^{\infty} \int_{r_3=|r_1-r_2|}^{r_1+r_2} r_1^a r_2^b r_3^c \times e^{-\lambda r_1 - \mu r_2} dr_1 dr_2 dr_3, \quad (25)$$

and the coefficients $C(a, b, c)$ are given by

$$r_1^f r_2^g r_3^h Y(r_1, r_2, r_3) Z(r_1, r_2, r_3) = \sum C(a, b, c) r_1^a r_2^b r_3^c. \quad (26)$$

It will be noted that some of the integrals to be evaluated contain powers of r_1 , r_2 , or r_3 in the denominator. Thus, there will be nonzero values of $C(a, b, c)$ for which a , b , or c are less than minus one. However, it is found in such cases that the integrand always contains a factor which reduces the order of the singularity in such

²² See Ref. 18, p. 189.

²³ B. Schiff and C. L. Pekeris, Phys. Rev. **134**, A638 (1964).

a way that the integral itself is finite. For example, all integrals with a factor of r_3^2 in the denominator are found to have a factor of $r_1 - r_2$ in the numerator.

When wave functions containing a large number of terms were used, a severe loss of accuracy was encountered in evaluating integrals of the form (22) with $\lambda = 2\xi$ in the case of the higher excited states. This loss of accuracy is due to cancellation between the various contributions to the sum $\sum C(a,b,c)I(a,b,c)$, and can be understood as follows. Let us refer to the "outer" or " p " electron as electron 1. If ξ is very much less than η , then in the region of greatest probability density, r_1 will be much greater than r_2 , and hence r_3 will be almost equal to r_1 . Thus the set of coordinates (r_1, r_2, r_3) is not the most suitable with which to express the wave function in this case. The difficulty was overcome by replacing the variable r_3 by the variable $\rho \equiv r_3 - r_1$. It was indeed found that for the states with low values of ξ , the coefficients of the terms with high powers of r_1 in the expansion of the wave function in the (r_1, r_2, ρ) scheme were considerably smaller than the corresponding coefficients in the (r_1, r_2, r_3) scheme. On evaluating the integrals (22) in the (r_1, r_2, ρ) scheme, the degree of cancellation was found to be small. Of course, this scheme has the disadvantage that powers of r_3 in the denominator can no longer be divided out, and hence a different table of integrals has to be used for each negative power of r_3 . The (r_1, r_2, r_3) scheme was still used, therefore, for the cases where no significant loss of accuracy occurred. The formulas for the integrals in the (r_1, r_2, ρ) scheme analogous to the $I(a,b,c)$ are given in Appendix B.

IV. THE NUMERICAL RESULTS

A. Nonrelativistic Eigenvalues

The nonrelativistic energy is given by the eigenvalue $E = -\epsilon^2$ of the Schrödinger equation (1). E is given in atomic units, and the corresponding ionization energy ν in units of cm^{-1} is calculated from E by means of the relation

$$\nu = -(2E + Z^2)R = (2\epsilon^2 - Z^2)R. \quad (27)$$

(In Refs. 1 and 12, this relation appears incorrectly with an extra factor of 2. The results listed are unaffected.) For the Rydberg constant R , we used the values $R_{\text{He}^+} = 109\,722.267 \text{ cm}^{-1}$ and $R_{\text{Li}^+} = 109\,728.727 \text{ cm}^{-1}$ for the helium atom and the lithium ion respectively. In the C scheme, computations were carried out for the 2^1P , 2^3P , 3^1P , and 3^3P states of helium, and up to $N = 220$ terms were included in the expansion of the wave function. The ionization energies ν obtained with $N = 84, 120, 165,$ and 220 for each of the four states have been listed in a previous publication (see Table I of Ref. 12) together with the results of an extrapolation to infinite order. By comparison with the extrapolated values, it is estimated that the values at order 220 have converged to within an accuracy varying from about 0.2 cm^{-1} for the 2^3P state to 2 cm^{-1} for the 3^3P state.

TABLE I. Nonrelativistic ionization energy ν of the 2^3P state in cm^{-1} . Comparison of results from C and D schemes.

Ω	N	C scheme	D scheme
3	20	29 166.766	29 210.757
4	35	29 200.862	29 221.312
5	56	29 213.953	29 221.792
6	84	29 219.015	29 222.096
7	120	29 220.944	29 222.133
8	165	29 221.676	29 222.148
9	220	29 221.958	29 222.152

In the D scheme, the eigenvalue is maximized with respect to the parameters ξ and η . In view of the interest in the fine-structure splitting of the 3^3P levels, this scheme was first applied to the 2^3P and 3^3P states of helium. The ionization energies obtained for the 2^3P level using the C and D schemes are compared in Table I, and it will be seen that the use of the D scheme leads to a considerable improvement in the results. We decided, therefore, to extend the D scheme computations up to order 560, corresponding to $\Omega = 13$. In view of the large amount of computer time required to calculate the value of a high order determinant, the optimization was only carried out up to order 120 (and also partially for order 165 in the case of the 2^3P state), the values of ξ and η for higher orders being estimated by extrapolation. This procedure is based on the observation that the eigenvalue is much more sensitive to changes in the number of terms in the expansion than to variations in the values of ξ and η , provided that these parameters are not allowed to vary too widely from their optimum values. To illustrate this point, in Table II we have listed the eigenvalues obtained for the 2^3P state for order 84 using various values of ξ and η in the vicinity of their optimal values. We have also listed the C-scheme eigenvalue as the first entry in the table. It will be seen that, aside from the C-scheme result, the poorest eigenvalue listed ($E = -2.1331638925$ with $\xi = 0.81$, $\eta = 1.85$) differs from the optimum ($E = -2.1331639282$ with $\xi = 0.8277$, $\eta = 1.96016$) by roughly 3.6×10^{-8} , whereas the optimum eigenvalues for order 56 ($E = -2.1331625437$ with $\xi = 0.7914$, $\eta = 2.0975$) and for

TABLE II. Nonrelativistic eigenvalues for the helium 2^3P state with 84 terms in the expansion using different values of the screening constants ξ and η .

ξ	η	$-E(\text{atomic units})$
0.51604... (C)	2	2.1331498878
0.81	1.85	2.1331638925
0.8	1.953	2.1331638940
0.81	1.87	2.1331639002
0.81	2	2.1331639099
0.81	1.92	2.1331639116
0.82	1.995	2.1331639225
0.82	1.953	2.1331639253
0.83	1.93	2.1331639258
0.83	1.986	2.1331639265
0.8325	1.96	2.1331639270
0.8277	1.96016	2.1331639282

TABLE III. Nonrelativistic eigenvalues for the 2^3P state of helium (in atomic units).

Ω	N	ξ	η	$-E$	Ω	N	ξ	η	$-E$
3	20	0.725	2.066	2.133112254831	4	35	0.77428	1.89513	2.133160354235
5	56	0.7914	2.0975	2.133162543742	6	84	0.8277	1.96016	2.133163928235
7	120	0.845	2.184	2.133164094685	8	165	0.895	2.1	2.133164164111
9	220	0.91	2.1	2.133164180840	10	286	0.95	2.1	2.133164187632
11	364	0.98	2.1	2.133164189423	12	455	1.01	2.1	2.133164190275
13	560	1.04	2.1	2.133164190534					
		Extrapolated (odd Ω)			2.133164190699	Extrapolated (even Ω)			2.133164190610

order 120 ($E = -2.1331640947$ with $\xi = 0.845$, $\eta = 2.184$) differ from the order 84 optimum by amounts of 1.4×10^{-6} and 1.7×10^{-7} , respectively. On the other hand, a much larger deviation of ξ from its optimal value leads to a considerable change in the eigenvalue, as is shown by the C-scheme result for order 84, which differs from the D-scheme optimum for this order by more than 1.4×10^{-5} .

TABLE IV. Nonrelativistic eigenvalues for the 3^3P state of helium (in atomic units).

Ω	N	ξ	$-E$	Ω	N	ξ	$-E$
3	20	0.4427	2.05793548553	4	35	0.45059	2.05800234939
5	56	0.505	2.05806853141	6	84	0.5135	2.05807451076
7	120	0.5465	2.05808014010	8	165	0.5556	2.05808058907
9	220	0.5756	2.05808099094	10	286	0.59	2.05808103540
11	364	0.615	2.05808107031	12	455	0.62	2.05808107688
13	560	0.65	2.05808108165				
Extrapolated (odd Ω)			2.05808108354	Extrapolated (even Ω)			2.05808108113

The optimum η for the 2^3P state was found to be close to the value $\eta = Z$ for all of the orders investigated, and we therefore decided to take $\eta = Z$ and to optimize with respect to ξ alone in all of the subsequent calculations. For a given state, the optimum value of ξ did not appear to vary smoothly with Ω , and the corresponding eigenvalues also showed an unsmooth behavior. However, the eigenvalues for odd values of Ω alone (i.e., for orders 20, 56, 120, ...) did vary smoothly, and a similar re-

mark applies to the results for even Ω alone. Tabulated in this way, the ratio of successive differences is quite small, taking on values between 0.09 and 0.18 for the highest orders considered. The eigenvalues have therefore been extrapolated, using the formula

$$E_{\text{extrapolated}} = E_1 + \frac{(E_1 - E_0)(E_2 - E_1)}{2E_1 - E_0 - E_2}, \quad (28)$$

where E_0 , E_1 , and E_2 are the values at order 220, 364, and 560 or at 165, 286, and 455 in the cases of odd and even Ω , respectively. The optimum values of the parameter ξ were also considered for the cases of even and odd Ω separately when estimating a suitable value of this parameter to use for the higher orders.

The eigenvalues obtained for the 2^3P and 3^3P states of helium are listed in Tables III and IV together with the optimum values of ξ (and of η in the case of 2^3P). The results for odd and even values of Ω have been tabulated separately. It will be noted that there is close agreement between the extrapolated values derived from consideration of the results for odd and for even Ω alone. We therefore decided to compute the eigenvalues for the remaining states to be considered using odd values of Ω only. The ionization energies obtained for the helium 2^1P , 2^3P , 3^1P , 3^3P , 4^1P , and 4^3P states and the 2^1P state of Li^+ are listed in Table V, together with the extrapolated values, which give some indication of the degree of convergence achieved. The final values used for the parameter ξ are listed in Table VI.

The only other published calculation of two-electron P -state wave functions of a comparable accuracy

TABLE V. Values of the nonrelativistic ionization energy ν in cm^{-1} .

Ω	N	He 2^1P	He 2^3P	He 3^1P	He 3^3P	He 4^1P	He 4^3P	Li^+ 2^1P
3	20	27 166.0159	29 210.7567	12 067.5681	12 713.6256	6788.7814	7034.0725	108 255.0048
5	56	27 176.0904	29 221.7924	12 097.1563	12 742.8218	6808.7740	7077.7571	108 268.9590
7	120	27 176.6404	29 222.1327	12 101.1159	12 745.3693	6816.2016	7090.9286	108 269.5269
9	220	27 176.6829	29 222.1516	12 101.5155	12 745.5560	6817.7406	7093.0844	108 269.5666
11	364	27 176.6876	29 222.1535	12 101.5599	12 745.5734	6818.0054	7093.3632	108 269.5708
13	560	27 176.6883	29 222.1537	12 101.5663	12 745.5759	6818.0520	7093.3965	
Extrapolated		27 176.6884	29 222.1538	12 101.5673	12 745.5763	6818.0620	7093.4011	108 269.5712

is that of Schwartz¹³ for the 2^3P state of helium. Schwartz used the fixed values $\xi=0.58$ and $\eta=2$ for the screening constants of the two electrons, and included terms with a factor of $(r_1+r_2)^{1/2}$ in the expansion of the wave function. The largest number of terms used in the expansion was 439, which gave an eigenvalue of -2.133164190626 , compared to the result of -2.133164190534 for order 560 obtained by the present authors. Schwartz's extrapolated value is -2.13316419080 , and thus lies 10^{-10} atomic units or $2 \times 10^{-5} \text{ cm}^{-1}$ deeper than our extrapolated value of -2.133164190699 for odd Ω .

B. The Total Ionization Energy

The results obtained for the total theoretical ionization energy $J_{\text{th}} = \nu - \epsilon_M + E_J$ are listed, in units of cm^{-1} ,

TABLE VI. Final values adopted for the screening constant ξ .

N	He 2^1P	He 2^3P	He 3^1P	He 3^3P	He 4^1P	He 4^3P	Li ⁺ 2^1P
20	0.696	0.725	0.398	0.4427	0.27	0.27	1.31
56	0.77	0.7914	0.4752	0.505	0.32	0.326	1.4471
120	0.834	0.845	0.528	0.5465	0.363	0.374	1.578
220	0.90	0.91	0.57	0.5756	0.40	0.406	1.70
364	0.96	0.98	0.61	0.615	0.435	0.44	1.835
560	1.02	1.04	0.65	0.65	0.47	0.475	

in Tables VII–XIII for all of the states considered, together with the corresponding values of ν , ϵ_M , E_2 , $C-5D/3$ (for 3P states) and E_J . In converting the three last-mentioned quantities from atomic units to cm^{-1} , we used the values $\alpha^2 R_{\text{He}^4} = 5.842755$ and $\alpha^2 R_{\text{Li}^7} = 5.843099$, while ϵ_M was computed using the values $2(m/M)R$

TABLE VII. The ionization energy and the expectation values of various operators for the 2^1P state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.123840361561	2.123842867892	2.123843061318	2.123843082754	2.123843085800
$\langle p_1^4 \rangle$ (a.u.)	40.1176220	40.1171446	40.1170497	40.1170208	40.1170114
$\langle \delta(\mathbf{r}_1) \rangle$ (a.u.)	1.27441973	1.27439914	1.27439472	1.27439326	1.27439295
$\langle \delta(\mathbf{r}_2) \rangle$ (a.u.)	0.00076470	0.00074386	0.00073805	0.00073626	0.00073562
$-E_2$ (cm^{-1})	0.2377800	0.2376289	0.2375884	0.2375769	0.2375736
$(2e^2-4)R_{\text{He}^4}$ (cm^{-1})	27 176.0904	27 176.6404	27 176.6829	27 176.6876	27 176.6883
$-\epsilon_M$ (cm^{-1})	-1.3855057	-1.3851637	-1.3851940	-1.3851971	-1.3851974
E_J (cm^{-1})	0.466673	0.467404	0.467624	0.467701	0.467717
J_{th} (cm^{-1})	27 175.1716	27 175.7226	27 175.7653	27 175.7701	27 175.7708
$\langle 1/r_1 \rangle$ (a.u.)	1.1231776734	1.1231775004	1.1231775084	1.1231775084	1.1231775097
$\langle r_1 \rangle$ (a.u.)	2.91031109	2.91064761	2.91067957	2.91068368	2.91068423
$\langle r_1^2 \rangle$ (a.u.)	15.756218	15.764634	15.765513	15.765634	15.765651
$\langle 1/r_2 \rangle$ (a.u.)	0.245029588	0.245024430	0.245023940	0.245023876	0.245023869
$\langle r_2 \rangle$ (a.u.)	5.1375846	5.1382552	5.1383189	5.1383270	5.1383281
$\langle r_2^2 \rangle$ (a.u.)	31.579783	31.596485	31.598234	31.598474	31.598508

TABLE VIII. The ionization energy and the expectation values of various operators for the 2^3P_1 state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.133162543742	2.133164094685	2.133164180840	2.133164189423	2.133164190534
$\langle p_1^4 \rangle$ (a.u.)	39.6476790	39.6482921	39.6483692	39.6483732	39.6483744
$\langle \delta(\mathbf{r}_1) \rangle$ (a.u.)	1.25880725	1.25884810	1.25885950	1.25886022	1.25886047
$-E_2$ (cm^{-1})	-0.40962053	-0.40992201	-0.40993580	-0.40993769	-0.40993800
$C-5D/3$ (cm^{-1})	0.0664061	0.0666466	0.0666287	0.0666227	0.0666223
$(2e^2-4)R_{\text{He}^4}$ (cm^{-1})	29 221.7924	29 222.1327	29 222.1516	29 222.1535	29 222.1537
$-\epsilon_M$ (cm^{-1})	1.9409794	1.9425442	1.9425888	1.9425883	1.9425884
E_J (cm^{-1})	-0.312826	-0.314095	-0.314739	-0.314788	-0.314803
J_{th} (cm^{-1})	29 223.4206	29 223.7611	29 223.7795	29 223.7813	29 223.7815
$\langle 1/r_1 \rangle$ (a.u.)	1.1332433490	1.1332424572	1.1332424189	1.1332424226	1.1332424224
$\langle r_1 \rangle$ (a.u.)	2.67369487	2.67394670	2.67396023	2.67396140	2.67396161
$\langle r_1^2 \rangle$ (a.u.)	13.2053933	13.2113357	13.2116982	13.2117329	13.2117393
$\langle 1/r_2 \rangle$ (a.u.)	0.266648440	0.266641645	0.266641335	0.266641313	0.266641309
$\langle r_2 \rangle$ (a.u.)	4.69942640	4.69992513	4.69995215	4.69995450	4.69995493
$\langle r_2^2 \rangle$ (a.u.)	26.630174	26.641987	26.642709	26.642778	26.642791

TABLE IX. The ionization energy and the expectation values of various operators for the 3^1P state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.0551262593	2.0551443030	2.0551461242	2.0551463263	2.0551463554
$\langle p_1^4 \rangle$ (a.u.)	40.045124	40.045739	40.045548	40.045525	40.045507
$\langle \delta(\mathbf{r}_1) \rangle$ (a.u.)	1.2735413	1.2736525	1.2736272	1.2736286	1.2736283
$\langle \delta(\mathbf{r}_3) \rangle$ (a.u.)	0.0003034	0.0002685	0.0002578	0.0002543	0.0002530
$-E_2$ (cm $^{-1}$)	0.079086	0.078462	0.078314	0.078279	0.078268
$(2e^2-4)R_{\text{He}^4}$ (cm $^{-1}$)	12 097.156	12 101.116	12 101.516	12 101.560	12 101.566
$-\epsilon_M$ (cm $^{-1}$)	-0.435292	-0.437431	-0.437668	-0.437678	-0.437668
E_J (cm $^{-1}$)	0.177618	0.171907	0.173448	0.173375	0.173380
J_{th} (cm $^{-1}$)	12 096.899	12 100.850	12 101.251	12 101.296	12 101.302
$\langle 1/r_1 \rangle$ (a.u.)	1.054967915	1.054972233	1.054972258	1.054972329	1.054972346
$\langle r_1 \rangle$ (a.u.)	6.672466	6.678473	6.679421	6.679530	6.679544
$\langle r_1^2 \rangle$ (a.u.)	91.5447	91.8202	91.8662	91.8719	91.8727
$\langle 1/r_3 \rangle$ (a.u.)	0.109623830	0.109601343	0.109597107	0.109596723	0.109596687
$\langle r_3 \rangle$ (a.u.)	12.623871	12.635868	12.637764	12.637983	12.638011
$\langle r_3^2 \rangle$ (a.u.)	183.1286	183.6810	183.7731	183.7846	183.7862

TABLE X. The ionization energy and the expectation values of various operators for the 3^3P_1 state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.0580685314	2.0580801401	2.0580809909	2.0580810703	2.0580810816
$\langle p_1^4 \rangle$ (a.u.)	39.914966	39.912292	39.912275	39.912301	39.912310
$\langle \delta(\mathbf{r}_1) \rangle$ (a.u.)	1.2693069	1.2691112	1.2691154	1.2691193	1.2691211
$-E_2$ (cm $^{-1}$)	-0.1196723	-0.1207475	-0.1208676	-0.1208816	-0.1208828
$C-5D/3$ (cm $^{-1}$)	0.016343	0.017461	0.017656	0.017680	0.017677
$(2e^2-4)R_{\text{He}^4}$ (cm $^{-1}$)	12 742.822	12 745.369	12 745.556	12 745.573	12 745.576
$-\epsilon_M$ (cm $^{-1}$)	0.544743	0.551844	0.552520	0.552588	0.552601
E_J (cm $^{-1}$)	-0.06300	-0.05640	-0.05668	-0.05688	-0.05699
J_{th} (cm $^{-1}$)	12 743.304	12 745.865	12 746.052	12 746.069	12 746.072
$\langle 1/r_1 \rangle$ (a.u.)	1.058043836	1.058024390	1.058022753	1.058022786	1.058022785
$\langle r_1 \rangle$ (a.u.)	6.3160668	6.3206196	6.3210987	6.3211210	6.3211269
$\langle r_1^2 \rangle$ (a.u.)	81.88872	82.08559	82.10822	82.10950	82.10982
$\langle 1/r_3 \rangle$ (a.u.)	0.115968200	0.115932519	0.115929096	0.115929018	0.115928987
$\langle r_3 \rangle$ (a.u.)	11.921071	11.930186	11.931144	11.931189	11.931201
$\langle r_3^2 \rangle$ (a.u.)	163.85846	164.25411	164.29952	164.30209	164.30274

TABLE XI. The ionization energy and the expectation values of various operators for the 4^1P state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.031027312	2.031061159	2.031068173	2.031069379	2.031069591
$\langle p_1^4 \rangle$ (a.u.)	40.02201	40.02231	40.02122	40.02131	40.02127
$\langle \delta(\mathbf{r}_1) \rangle$ (a.u.)	1.273252	1.273493	1.273382	1.273409	1.273405
$\langle \delta(\mathbf{r}_3) \rangle$ (a.u.)	0.0001569	0.0001316	0.0001198	0.0001149	0.0001129
$-E_2$ (cm $^{-1}$)	0.034160	0.034169	0.034145	0.034122	0.034110
$(2e^2-4)R_{\text{He}^4}$ (cm $^{-1}$)	6808.774	6816.202	6817.741	6818.005	6818.052
$-\epsilon_M$ (cm $^{-1}$)	-0.182383	-0.186699	-0.187862	-0.188132	-0.188165
E_J (cm $^{-1}$)	0.09182	0.07588	0.08124	0.07975	0.07997
J_{th} (cm $^{-1}$)	6808.683	6816.091	6817.634	6817.897	6817.944
$\langle 1/r_1 \rangle$ (a.u.)	1.0309996	1.0309985	1.0310004	1.0310005	1.0310004
$\langle r_1 \rangle$ (a.u.)	11.93075	11.94160	11.94592	11.94721	11.94759
$\langle r_1^2 \rangle$ (a.u.)	302.649	303.572	303.923	304.026	304.057
$\langle 1/r_3 \rangle$ (a.u.)	0.06185719	0.06186554	0.06186428	0.06186266	0.06186191
$\langle r_3 \rangle$ (a.u.)	23.12776	23.14932	23.15794	23.16050	23.16126
$\langle r_3^2 \rangle$ (a.u.)	605.332	607.171	607.872	608.078	608.139

TABLE XII. The ionization energy and the expectation values of various operators for the 4^3P_1 state of helium. a.u. stands for atomic units.

N	56	120	220	364	560
Ω	5	7	9	11	13
$-E$ (a.u.)	2.032253057	2.032313079	2.032322903	2.032324173	2.032324325
$\langle p_1^4 \rangle$ (a.u.)	39.965632	39.964963	39.966209	39.966295	39.966317
$\langle \delta(r_1) \rangle$ (a.u.)	1.2715848	1.2714621	1.2715479	1.2715397	1.2715387
$-E_2$ (cm ⁻¹)	-0.045035	-0.049133	-0.050123	-0.050322	-0.050352
$C-5D/3$ (cm ⁻¹)	0.004626	0.006378	0.006963	0.007141	0.007179
$(2e^2-4)R_{He^4}$ (cm ⁻¹)	7077.757	7090.929	7093.084	7093.363	7093.397
$-\epsilon_M$ (cm ⁻¹)	0.199044	0.221029	0.226298	0.227170	0.227279
E_J (cm ⁻¹)	-0.01932	-0.01461	-0.01767	-0.01684	-0.01669
J_{th} (cm ⁻¹)	7077.937	7091.135	7093.293	7093.574	7093.607
$\langle 1/r_1 \rangle$ (a.u.)	1.0322673	1.0322926	1.0322889	1.0322888	1.0322886
$\langle r_1 \rangle$ (a.u.)	11.42893	11.45556	11.46652	11.46823	11.46858
$\langle r_1^2 \rangle$ (a.u.)	277.073	278.994	279.769	279.899	279.926
$\langle 1/r_3 \rangle$ (a.u.)	0.06460254	0.06454418	0.06451133	0.06450670	0.06450572
$\langle r_3 \rangle$ (a.u.)	22.12820	22.18138	22.20326	22.20669	22.20738
$\langle r_3^2 \rangle$ (a.u.)	554.199	558.034	559.581	559.841	559.895

TABLE XIII. The ionization energy and the expectation values of various operators for the 2^1P state of the Li⁺ ion. a.u. stands for atomic units.

Ω	56	120	220	364
Ω	5	7	9	11
$-E$ (a.u.)	4.9933482870	4.9933508749	4.9933510558	4.9933510746
$\langle p_1^4 \rangle$ (a.u.)	204.14771	204.14637	204.14604	204.14594
$\langle \delta(r_1) \rangle$ (a.u.)	4.30659110	4.30657103	4.30657111	4.30657134
$\langle \delta(r_3) \rangle$ (a.u.)	0.0099987	0.0098816	0.0098520	0.0098429
$-E_2$ (cm ⁻¹)	2.22345	2.22272	2.22257	2.22254
$(2e^2-9)R_{Li^+}$ (cm ⁻¹)	108 268.9590	108 269.5269	108 269.5666	108 269.5708
$-\epsilon_M$ (cm ⁻¹)	-4.3111022	-4.3110606	-4.3110638	-4.3110642
E_J (cm ⁻¹)	5.63407	5.63593	5.63591	5.63587
J_{th} (cm ⁻¹)	108 270.2820	108 270.8518	108 270.8914	108 270.8956
$\langle 1/r_1 \rangle$ (a.u.)	1.746578823	1.746579487	1.746579531	1.746579541
$\langle r_1 \rangle$ (a.u.)	1.52187696	1.52192741	1.52193161	1.52193201
$\langle r_1^2 \rangle$ (a.u.)	4.0408638	4.0415579	4.0416206	4.0416271
$\langle 1/r_3 \rangle$ (a.u.)	0.492779764	0.492775482	0.492775131	0.492775102
$\langle r_3 \rangle$ (a.u.)	2.5923595	2.5924596	2.5924679	2.5924687
$\langle r_3^2 \rangle$ (a.u.)	8.072704	8.074071	8.074195	8.074208

TABLE XIV. Two-electron P -state ionization energies, comparison between theory and experiment. ν is the nonrelativistic ionization energy in cm⁻¹, and J_{th} the total theoretical ionization energy including the mass polarization and relativistic corrections. The results tabulated are for $N=560$ in the case of helium, and $N=364$ in the case of Li⁺. J_{exp} is the experimental value.

	He 2^1P	He 2^3P_1	He 3^1P	He 3^3P_1	He 4^1P	He 4^3P_1	Li ⁺ 2^1P
ν	27 176.69	29 222.15	12 101.57	12 745.58	6818.05	7093.40	108 269.57
J_{th}	27 175.77	29 223.78	12 101.30	12 746.07	6817.94	7093.61	108 270.90
J_{exp}	27 175.81 ^a	29 223.86 ^a	12 101.33 ^a	12 746.13 ^b	6817.99 ^b	7093.67 ^c	108 270.81 ^d
$J_{exp}-J_{th}$	+0.04	+0.08	+0.03	+0.06	+0.05	+0.06	-0.09

^a Reference 8.^b Reference 24.^c See Ref. 24. We have assumed that the term value listed by Martin corresponds to the $J=1$ level.^d Reference 9.

= 30.08387 for He⁴ and $2(m/M)R=17.163109$ for Li⁷. None of these constants are known to such an accuracy, and the results are only quoted in Tables VII–XIII to the number of significant figures given in order to exhibit

the rate of convergence in cm⁻¹, and to enable the original values in atomic units to be recovered if desired. The values of these constants are, however, known sufficiently accurately to enable E_J and ϵ_M to be

computed in cm^{-1} to at least four places after the decimal point in all cases, an accuracy sufficient for the present calculations. The tables also contain the values of $-E = \epsilon^2$ and the expectation values of p_1^4 , $\delta(\mathbf{r}_1)$, $\delta(\mathbf{r}_3)$, $1/r_1$, r_1 , r_1^2 , $1/r_3$, r_3 , and r_3^2 in atomic units. It will be seen that at $N=560$ (or $N=364$ in the case of Li^+), J_{th} has converged to within an accuracy of 10^{-4} – 10^{-2} cm^{-1} , and is thus in all cases subject to an estimated uncertainty less than that of experiment. The results are compared with those of experiment in Table XIV,²⁴ in which we have listed ν and J_{th} for the highest value of N in the case of each of the states considered, together with the experimental value J_{exp} . The difference $J_{\text{exp}} - J_{\text{th}}$ is presumably accounted for by the contributions from the radiative terms, and is less than 0.1 cm^{-1} in absolute magnitude in all cases.

There have been no calculations of the relativistic corrections for a two-electron P state with which we may compare the results presently described, apart from Schwartz's calculation¹³ of the fine-structure splitting of the helium 2^3P level. The splitting is obtained by evaluating $\langle H_3 + H_3 \rangle$ [see Eq. (A33)], and our results have been compared with those of Schwartz in a previous publication,¹ in which the excellent agreement between the results of the two calculations is demonstrated. Our results for the mass polarization correction ϵ_M agree well with the values of 1.3874 and -1.9443 cm^{-1} obtained for the 2^1P and 2^3P states of helium by Araki *et al.*,²⁵ and also with the values of 1.383 and -1.942 cm^{-1} which may be derived from the results of recent calculations by Machacek *et al.*²⁶ for these two states.

Our result for the Li^+ ion confirms the identification of the line at 9581.42 \AA as belonging to the 2^1S – 2^1P transition.¹⁵ Combining our value of $J_{\text{th}} = 108270.89 \text{ cm}^{-1}$ for the 2^1P level with the theoretical ionization energy of $118\,704.88 \text{ cm}^{-1}$ obtained by one of us for the 2^1S level,¹⁴ we obtain the value $10\,433.99 \text{ cm}^{-1}$ for the 2^1S – 2^1P transition. This is in excellent agreement with Toresson and Edlén's experimental value of $10\,434.01 \pm 0.10 \text{ cm}^{-1}$.¹⁵

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²⁵ G. Araki, K. Mano, and M. Ohta, Phys. Rev. **115**, 1222 (1959).

²⁶ M. Machacek, F. C. Sanders, and C. W. Scherr, Phys. Rev. **136**, A680 (1964); **137**, A1066 (1965). See also: C. W. Scherr and M. Machacek, *ibid.* **138**, A371 (1965).

APPENDIX A: INTEGRATION OVER THE ANGULAR VARIABLES

I. Mass Polarization

We have to evaluate $\int \nabla_1 \psi \cdot \nabla_2 \psi d\tau$. We write $F(r_1, r_2, \theta) = r_1 G(r_1, r_2, \theta)$. Then the wave function (4) may be written in the form $\psi = z_1 G \pm z_2 \tilde{G}$, so that

$$\nabla_1 \psi = z_1 \nabla_1 G \pm z_2 \nabla_1 \tilde{G} + G \hat{z}, \quad (\text{A1})$$

where \hat{z} is the unit vector in the z direction. $\nabla_2 \psi$ may be expressed similarly, and thus

$$\begin{aligned} \int \nabla_1 \psi \cdot \nabla_2 \psi d\tau = \int \left\{ 2z_1^2 \nabla_1 G \cdot \nabla_2 G \right. \\ \left. + 2z_2 \tilde{G} \frac{\partial \tilde{G}}{\partial z_1} \pm \left(G \tilde{G} + 2z_1 \tilde{G} \frac{\partial G}{\partial z_1} - z_1 z_2 \nabla_1 G \cdot \nabla_2 \tilde{G} \right. \right. \\ \left. \left. + z_1 z_2 \nabla_1 \tilde{G} \cdot \nabla_2 G \right) \right\} d\tau, \quad (\text{A2}) \end{aligned}$$

where we have made use of the fact that certain terms give equal contributions when integrated, because of the symmetry of the region of integration with respect to the two electrons. We now transform the derivatives into the $r_1, r_2, \theta, \theta', \phi', \phi$ scheme, using the equations

$$\cos \theta_2 = \cos \theta' \cos \theta - \sin \theta' \sin \theta \cos \phi, \quad (\text{A3})$$

$$\frac{\partial}{\partial z_1} f(r_1, r_2, \theta) = \cos \theta' \frac{\partial f}{\partial r_1} + \frac{\sin \theta' \cos \phi}{r_1} \frac{\partial f}{\partial \theta}, \quad (\text{A4})$$

where $\partial f / \partial r_1$ denotes the derivative with r_2 and θ held constant, and $\partial f / \partial \theta$ similarly. Since G is a function of r_1, r_2 and θ only, the scalar products occurring in (A2) will be independent of the angular variables θ', ϕ', ϕ , and we can thus integrate immediately over these variables to obtain

$$\begin{aligned} \int \nabla_1 \psi \cdot \nabla_2 \psi d\tau = \frac{8\pi^2}{3} \int \left\{ 2r_1^2 \nabla_1 G \cdot \nabla_2 G \right. \\ \left. + 2r_2 \cos \theta \tilde{G} \frac{\partial \tilde{G}}{\partial r_1} - 2 \frac{r_2 \sin \theta}{r_1} \tilde{G} \frac{\partial \tilde{G}}{\partial \theta} \pm \left[3G \tilde{G} + 2r_1 \tilde{G} \frac{\partial G}{\partial r_1} + r_1 r_2 \right. \right. \\ \left. \left. \times \cos \theta (\nabla_1 G \cdot \nabla_2 \tilde{G} + \nabla_1 \tilde{G} \cdot \nabla_2 G) \right] \right\} dV, \quad (\text{A5}) \end{aligned}$$

where $dV = r_1^2 r_2^2 \sin \theta dr_1 dr_2 d\theta = r_1 r_2 r_3 dr_1 dr_2 dr_3$. By taking suitable axes in the r_1, r_2, θ plane, one can easily show that the scalar product of the gradients of any two functions of r_1, r_2 , and θ alone may be written

$$\begin{aligned} \nabla_1 f(r_1, r_2, \theta) \cdot \nabla_2 g(r_1, r_2, \theta) \\ = \left(\frac{\partial f}{\partial r_1} \frac{\partial g}{\partial r_2} - \frac{1}{r_1 r_2} \frac{\partial f}{\partial \theta} \frac{\partial g}{\partial \theta} \right) \cos \theta \\ - \left(\frac{1}{r_1} \frac{\partial f}{\partial \theta} \frac{\partial g}{\partial r_2} + \frac{1}{r_2} \frac{\partial f}{\partial r_1} \frac{\partial g}{\partial \theta} \right) \sin \theta. \quad (\text{A6}) \end{aligned}$$

If we substitute $G(r_1, r_2, \theta) = e^{-\xi r_1 - \eta r_2} M(r_1, r_2, r_3)$ and transform from (r_1, r_2, θ) to (r_1, r_2, r_3) , the integral may finally be written, after some algebra, in the form

$$\begin{aligned} \int \nabla_1 \psi \cdot \nabla_2 \psi d\tau = & \frac{8\pi^2}{3} \int \{r_1^2 r_3 t_3 M_1 M_2 - (r_1^2 r_2 t_2 M_1 + r_1^3 t_1 M_2 + 2r_1^3 r_2 r_3 M_3) M_3 \\ & + M[-\eta r_1^2 r_3 t_3 M_1 + (r_1 r_3 t_3 - \xi r_1^2 r_3 t_3) M_2 + (\xi r_1^2 r_2 t_2 + \eta r_1^3 t_1 - r_1 r_2 t_2) M_3 + (\xi \eta r_1^2 r_3 t_3 - \eta r_1 r_3 t_3) M]\} \\ & \times e^{-2\xi r_1 - 2\eta r_2} dr_1 dr_2 dr_3 \pm \frac{2\pi^2}{3} \int \{M_1(r_3 t_3^2 \tilde{M}_2 - 2r_2 t_2 t_3 \tilde{M}_3) + M_2(r_3 t_3^2 \tilde{M}_1 - 2r_1 t_1 t_3 \tilde{M}_3) - 4r_1 r_2 t_2 t_3 (r_3)^{-1} M_3 \tilde{M}_3 \\ & + \tilde{M}[(8r_1^2 r_2 r_3 - 2\xi r_3 t_3^2) M_1 - 2\eta r_3 t_3^2 M_2 + (4r_1 r_2 t_2 + 2\xi r_1 t_1 t_3 + 2\eta r_2 t_2 t_3) M_3 \\ & + (12r_1 r_2 r_3 - 8\xi r_1^2 r_2 r_3 + \xi^2 r_3 t_3^2 + \eta^2 r_3 t_3^2) M]\} e^{-(\xi+\eta)(r_1+r_2)} dr_1 dr_2 dr_3, \quad (A7) \end{aligned}$$

where M_1 denotes $\partial M / \partial r_1$, and so on, and $t_1 = -r_1^2 + r_2^2 + r_3^2$, $t_2 = r_1^2 - r_2^2 + r_3^2$, and $t_3 = r_1^2 + r_2^2 - r_3^2$. We have expressed the integral in this form, as a sum of integrals of the type (22), in view of the fact that an interpretive programming scheme has been developed for evaluating integrals of this type on the computer.

II. $\langle p_1^4 \rangle$

We have

$$\langle p_1^4 \rangle = \int (\nabla_1^2 \psi)^2 d\tau = \frac{1}{2} \int [(\nabla_1^2 \psi)^2 + (\nabla_2^2 \psi)^2] d\tau. \quad (A8)$$

From the wave equation (1), it follows that

$$(\nabla_1^2 \psi)^2 + (\nabla_2^2 \psi)^2 = -2\nabla_1^2 \psi \cdot \nabla_2^2 \psi + 4[E - V]^2 \psi^2, \quad (A9)$$

where $V = -Z/r_1 - Z/r_2 + 1/r_3$, so that

$$-\langle p_1^4 \rangle = \int \nabla_1^2 \psi \cdot \nabla_2^2 \psi d\tau - 2 \int (E - V)^2 \psi^2 d\tau = I - 2J. \quad (A10)$$

The evaluation of J is very simple. Again writing $\psi = z_1 G \pm z_2 \tilde{G}$ and integrating over the variables θ' , ϕ' , ϕ we obtain the result

$$J = \frac{16\pi^2}{3} \int \left\{ E^2 + \frac{Z^2}{r_1^2} + \frac{Z^2}{r_2^2} + \frac{1}{r_3^2} + \frac{2EZ}{r_1} + \frac{2EZ}{r_2} + \frac{2E}{r_3} + \frac{2Z^2}{r_1 r_2} + \frac{2Z}{r_1 r_3} + \frac{2Z}{r_2 r_3} \right\} (r_1^2 G^2 \pm r_1 r_2 G \tilde{G} \cos \theta) dV, \quad (A11)$$

which is then converted into the r_1, r_2, r_3 scheme. To evaluate I , we note that

$$\nabla_1^2 \psi = z_1 \nabla_1^2 G \pm z_2 \nabla_1^2 \tilde{G} + 2(\partial G / \partial z_1) \quad (A12)$$

and $\nabla_2^2 \psi$ similarly, so that

$$I = \int \left\{ 2z_1^2 \nabla_1^2 G \cdot \nabla_2^2 G + 4z_1 \frac{\partial G}{\partial z_1} \nabla_2^2 G \right\} d\tau \pm \int \left\{ z_1 z_2 (\nabla_1^2 G \cdot \nabla_2^2 \tilde{G} + \nabla_1^2 \tilde{G} \cdot \nabla_2^2 G) + 4 \frac{\partial G}{\partial z_1} \frac{\partial \tilde{G}}{\partial z_2} + 4z_2 \nabla_2^2 \tilde{G} \frac{\partial G}{\partial z_1} \right\} d\tau. \quad (A13)$$

Using (A3), (A4), and the relation

$$\frac{\partial}{\partial z_2} f(r_1, r_2, \theta) = (\cos \theta' \cos \theta - \sin \theta' \sin \theta \cos \phi) \frac{\partial f}{\partial r_2} - \frac{(\cos \theta' \sin \theta + \sin \theta' \cos \theta \cos \phi)}{r_2} \frac{\partial f}{\partial \theta}, \quad (A14)$$

and making use of the fact that $\nabla_1^2 f(r_1, r_2, \theta)$ and $\nabla_2^2 f(r_1, r_2, \theta)$ are independent of θ' , ϕ' , and ϕ , we may integrate over these angles to obtain the result

$$\begin{aligned} I = & \frac{16\pi^2}{3} \int \left\{ r_1^2 \nabla_1^2 G + 2r_1 \frac{\partial G}{\partial r_1} \right\} \nabla_2^2 G dV \pm \frac{4\pi^2}{3} \int \left\{ \left[2r_1 r_2 \cos \theta \nabla_1^2 G + 8r_2 \cos \theta \frac{\partial G}{\partial r_1} - \frac{8r_2 \sin \theta}{r_1} \frac{\partial G}{\partial \theta} \right] \nabla_2^2 \tilde{G} \right. \\ & \left. + 8 \cos \theta \frac{\partial G}{\partial r_1} \frac{\partial \tilde{G}}{\partial r_2} - \frac{8 \cos \theta}{r_1 r_2} \frac{\partial G}{\partial \theta} \frac{\partial \tilde{G}}{\partial \theta} - \frac{16 \sin \theta}{r_2} \frac{\partial G}{\partial r_1} \frac{\partial \tilde{G}}{\partial \theta} + 2r_1 r_2 \cos \theta \nabla_1^2 \tilde{G} \cdot \nabla_2^2 G \right\} dV. \quad (A15) \end{aligned}$$

Writing $G(r_1, r_2, \theta) = e^{-\xi r_1 - \eta r_2} M(r_1, r_2, r_3)$ and going over to r_1, r_2, r_3 making use of the relation

$$\nabla_1^2 M(r_1, r_2, r_3) = \frac{\partial^2 M}{\partial r_1^2} + \frac{t_2}{r_1 r_3} \frac{\partial^2 M}{\partial r_1 \partial r_3} + \frac{\partial^2 M}{\partial r_3^2} + \frac{2}{r_1} \frac{\partial M}{\partial r_1} + \frac{2}{r_3} \frac{\partial M}{\partial r_3} \quad (\text{A16})$$

and a similar relation for $\nabla_2^2 M(r_1, r_2, r_3)$ we obtain the final result

$$\begin{aligned} -\langle p_1^4 \rangle = I - 2J = \frac{16\pi^2}{3} \int & [(r_3)^{-1} \{ r_1^3 r_3 M_{11} + (4r_1^2 r_3 - 2\xi r_1^3 r_3) M_1 + r_1^3 r_3 M_{33} + r_1^2 t_2 M_{13} + (2r_1^3 + r_1 t_2 - \xi r_1^2 t_2) M_3 \\ & + (\xi^2 r_1^3 r_3 - 4\xi r_1^2 r_3) M \} \{ r_2 r_3 M_{22} + t_1 M_{23} + r_2 r_3 M_{33} + (2r_3 - 2\eta r_2 r_3) M_2 + (2r_2 - \eta t_1) M_3 + (\eta^2 r_2 r_3 - 2\eta r_3) M \} \\ & + r_1 (r_2 r_3)^{-1} \{ -2E^2 r_1^2 r_2^2 r_3^2 - 2Z^2 r_2^2 r_3^2 - 2Z^2 r_1^2 r_3^2 - 2r_1^2 r_2^2 - 4ZE r_1 r_2^2 r_3^2 - 4ZE r_1^2 r_2 r_3^2 + 4E r_1^2 r_2^2 r_3 \\ & - 4Z^2 r_1 r_2 r_3^2 + 4Z r_1 r_2^2 r_3 + 4Z r_1^2 r_2 r_3 \} M^2] e^{-2\xi r_1 - 2\eta r_2} dr_1 dr_2 dr_3 \pm \frac{4\pi^2}{3} \int [(r_3)^{-1} \{ r_1 r_3 t_3 M_{11} + t_2 t_3 M_{13} + r_1 r_3 t_3 M_{33} \\ & + (6r_3 t_3 - 2\xi r_1 r_3 t_3) M_1 + (6r_1 t_3 - 8r_1 r_2^2 - \xi t_2 t_3) M_3 + (\xi^2 r_1 r_3 t_3 - 6\xi r_3 t_3) M \} \{ r_2 r_3 \tilde{M}_{22} + t_1 \tilde{M}_{23} + r_2 r_3 \tilde{M}_{33} \\ & + (2r_3 - 2\xi r_2 r_3) \tilde{M}_2 + (2r_2 - \xi t_1) \tilde{M}_3 + (\xi^2 r_2 r_3 - 2\xi r_3) \tilde{M} \} + (r_3)^{-1} \{ r_2 r_3 t_3 M_{22} + t_1 t_3 M_{23} + r_2 r_3 t_3 M_{33} \\ & + (2r_3 t_3 - 2\eta r_2 r_3 t_3) M_2 + (2r_2 t_3 - \eta t_1 t_3) M_3 + (\eta^2 r_2 r_3 t_3 - 2\eta r_3 t_3) M \} \{ r_1 r_3 \tilde{M}_{11} + t_2 \tilde{M}_{13} + r_1 r_3 \tilde{M}_{33} + (2r_3 - 2\eta r_1 r_3) \tilde{M}_1 \\ & + (2r_1 - \eta t_2) \tilde{M}_3 + (\eta^2 r_1 r_3 - 2\eta r_3) \tilde{M} \} + \{ 4r_3 t_3 M_1 - 8r_1 t_1 M_3 - 4\xi r_3 t_3 M \} \{ \tilde{M}_2 - \xi \tilde{M} \} - 8r_1 r_2 t_2 (r_3)^{-1} M_3 \tilde{M}_1 \\ & + (r_1 r_2 r_3)^{-1} \{ -4E^2 r_1^2 r_2^2 r_3^2 t_3 - 4Z^2 r_2^2 r_3^2 t_3 - 4Z^2 r_1^2 r_3^2 t_3 - 4r_1^2 r_2^2 t_3 - 8ZE r_1 r_2^2 r_3^2 t_3 - 8ZE r_1^2 r_2 r_3^2 t_3 + 8E r_1^2 r_2^2 r_3 t_3 \\ & - 8Z^2 r_1 r_2 r_3^2 t_3 + 8Z r_1 r_2^2 r_3 t_3 + 8Z r_1^2 r_2 r_3 t_3 \} M \tilde{M}] e^{-(\xi+\eta)(r_1+r_2)} dr_1 dr_2 dr_3. \quad (\text{A17}) \end{aligned}$$

Again, we have written this integral in a form corresponding as closely as possible to that represented in the computer program.

III. E_2

The complicated nature of the angular dependence of the operator H_2 necessitated the development of a general method for integrating over the angular variables. We shall outline the method in some detail, in view of its possible usefulness in other cases. Instead of, as heretofore, writing down the operators using the set of variables $(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$ and then transforming into the set $(r_1, r_2, r_3, \theta', \phi', \phi)$, we shall write the operators directly in terms of the latter set of coordinates. It will be remembered that r_1, r_2 and r_3 define the shape of the triangle formed by the nucleus and the two electrons, and $\theta', \phi',$ and ϕ are the Eulerian angles describing the orientation of this triangle

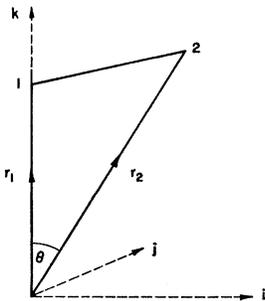


FIG. 2. The coordinate system used in computing E_2 .

with respect to a set of space axes x, y, z (see Fig. 1).

In order to evaluate the scalar products, it is easiest to resolve the various vectors into components in the r_1, r_2 plane and perpendicular to it. We therefore take a set of rectangular Cartesian coordinates with unit vectors \mathbf{k} along r_1, \mathbf{j} perpendicular to the r_1, r_2 plane, and \mathbf{i} in this plane in such a way that $\mathbf{i}, \mathbf{j}, \mathbf{k}$ form a right-handed orthogonal set, as shown in Fig. 2. This set may be brought into coincidence with the space axes x, y and z by successive rotations of $-\phi$ about the \mathbf{k} axis, $-\theta'$ about the (new) \mathbf{j} axis, and $-\phi'$ about the (new) \mathbf{k} axis again. Thus it is easily shown that the compo-

nents of \mathbf{i} , \mathbf{j} and \mathbf{k} with respect to the space axes x , y and z are

$$\begin{aligned}\mathbf{i} &= (\cos\theta' \cos\phi \cos\phi' - \sin\phi \sin\phi', \cos\theta' \cos\phi \sin\phi' + \sin\phi \cos\phi', -\sin\theta' \cos\phi), \\ \mathbf{j} &= (-\cos\theta' \sin\phi \cos\phi' - \cos\phi \sin\phi', -\cos\theta' \sin\phi \sin\phi' + \cos\phi \cos\phi', \sin\theta' \sin\phi), \\ \mathbf{k} &= (\sin\theta' \cos\phi', \sin\theta' \sin\phi', \cos\theta').\end{aligned}\quad (\text{A18})$$

The vectors which will be needed in the calculation may be expressed in terms of their components along the \mathbf{i} , \mathbf{j} , and \mathbf{k} axes as follows:

$$\begin{aligned}\mathbf{r}_1 &= \{0, 0, r_1\}, \\ \mathbf{r}_2 &= \{r_2 \sin\theta, 0, r_2 \cos\theta\}, \\ \mathbf{r}_3 &= \{r_2 \sin\theta, 0, r_2 \cos\theta - r_1\},\end{aligned}$$

$$\nabla_1 = \left\{ \frac{\cos\phi}{r_1} \frac{\partial}{\partial\theta'} + \frac{\sin\phi}{r_1 \sin\theta'} \frac{\partial}{\partial\phi'}, \frac{\cot\theta' \sin\phi}{r_1} \frac{\partial}{\partial\phi} + \frac{r_2 \sin\theta}{r_3} \frac{\partial}{\partial r_3}, \right. \\ \left. - \frac{\sin\phi}{r_1} \frac{\partial}{\partial\theta'} + \frac{\cos\phi}{r_1 \sin\theta'} \frac{\partial}{\partial\phi'} - \frac{(\cot\theta + \cot\theta' \cos\phi)}{r_1} \frac{\partial}{\partial\phi}, \frac{\partial}{\partial r_1} + \frac{(r_1 - r_2 \cos\theta)}{r_3} \frac{\partial}{\partial r_3} \right\}$$

and

$$\nabla_2 = \left\{ \sin\theta \frac{\partial}{\partial r_2} + \frac{r_2 \sin\theta}{r_3} \frac{\partial}{\partial r_3}, \frac{1}{r_2 \sin\theta} \frac{\partial}{\partial\phi}, \cos\theta \frac{\partial}{\partial r_2} + \frac{(r_2 \cos\theta - r_1)}{r_3} \frac{\partial}{\partial r_3} \right\}.\quad (\text{A19})$$

We note that the gradients of any function of r_1 , r_2 , and r_3 alone lie in the $\mathbf{r}_1, \mathbf{r}_2$ plane, as we should expect. It will be seen that the expressions for the various components of the vectors contain terms involving $\cos\theta$ and $\sin\theta$. These have just been inserted as a shorthand notation for the corresponding functions of r_1, r_2, r_3 [e.g., $\cos\theta$ has been written for $(r_1^2 + r_2^2 - r_3^2)/(2r_1 r_2)$]. It is useful to retain them throughout part of the subsequent development, rather than to perform the tedious algebra which would result if the variable θ were to be eliminated completely at this stage. Expressions involving θ do not, of course, commute with the operation of differentiation with respect to r_1, r_2 , or r_3 , and the following relations are useful in this connection

$$\begin{aligned}\frac{\partial}{\partial r_1} \cos\theta &= \frac{t_2}{2r_1^2 r_2}, & \frac{\partial}{\partial r_2} \cos\theta &= \frac{t_1}{2r_1 r_2^2}, & \frac{\partial}{\partial r_3} \cos\theta &= \frac{-r_3}{r_1 r_2}, \\ \frac{\partial}{\partial r_1} \sin\theta &= -\frac{t_2 \cot\theta}{2r_1^2 r_2}, & \frac{\partial}{\partial r_2} \sin\theta &= -\frac{t_1 \cot\theta}{2r_1 r_2^2}, & \frac{\partial}{\partial r_3} \sin\theta &= \frac{r_3 \cot\theta}{r_1 r_2},\end{aligned}\quad (\text{A20})$$

where $\partial/\partial r_1$ denotes differentiation with respect to r_1 keeping r_2, r_3, θ', ϕ' , and ϕ constant, and so on.

We note that $E_2 = \alpha^2 X$, where

$$X = \frac{1}{2} \left\langle \frac{\nabla_1 \cdot \nabla_2}{r_3} + \frac{\mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_2) \cdot \nabla_1}{r_3^3} \right\rangle = \int (F \cos\theta_1 \pm \tilde{F} \cos\theta_2) \left\{ \frac{\nabla_2}{r_3} + \frac{\mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_2)}{r_3^3} \right\} \cdot \nabla_1 F \cos\theta_1 d\tau.\quad (\text{A21})$$

Writing $F(r_1, r_2, \theta) \equiv H(r_1, r_2, r_3)$ and using the formulas (A19), we see that the vector $\nabla_1(F \cos\theta_1)$ may be written

$$\begin{aligned}\nabla_1(F \cos\theta_1) &= \cos\theta' \nabla_1 H + H \left\{ -\frac{\sin\theta' \cos\phi}{r_1}, \frac{\sin\theta' \sin\phi}{r_1}, 0 \right\} \\ &= \left\{ -\frac{r_2 \sin\theta \cos\theta'}{r_3} \frac{\partial H}{\partial r_3} - \frac{H \sin\theta' \cos\phi}{r_1}, \frac{H \sin\theta' \sin\phi}{r_1}, \cos\theta' \frac{\partial H}{\partial r_1} + \frac{(r_1 - r_2 \cos\theta)}{r_3} \cos\theta' \frac{\partial H}{\partial r_3} \right\}.\end{aligned}\quad (\text{A22})$$

Similarly, the operator $\nabla_2/r_3 + \mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_2)/r_3^3$ may be written

$$\left\{ \frac{(3r_3^2 + r_2^2 - r_1^2)}{2r_3^3} \sin\theta \frac{\partial}{\partial r_2} + \frac{2r_2 \sin\theta}{r_3^2} \frac{\partial}{\partial r_3}, \frac{1}{r_2 r_3 \sin\theta} \frac{\partial}{\partial\phi}, \frac{(2r_3^2 \cos\theta - r_1 r_2 \sin^2\theta)}{r_3^3} \frac{\partial}{\partial r_2} + \frac{2(r_2 \cos\theta - r_1)}{r_3^2} \frac{\partial}{\partial r_3} \right\}.\quad (\text{A23})$$

Thus, taking the scalar product of (A23) and (A22) and making use of the relations (A20), and the fact that

$\partial \mathbf{i} / \partial \phi = \mathbf{j}$, $\partial \mathbf{j} / \partial \phi = -\mathbf{i}$, and $\partial \mathbf{k} / \partial \phi = 0$, we have, after some algebra, the result

$$\begin{aligned} \{\nabla_2 / r_3 + \mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_2) / r_3^3\} \cdot \nabla_1 F \cos \theta_1 = \cos \theta' \left\{ \left(\frac{2 \cos \theta}{r_3} - \frac{r_1 r_2 \sin^2 \theta}{r_3^3} \right) \frac{\partial^2 H}{\partial r_1 \partial r_2} + \frac{2(r_2 \cos \theta - r_1)}{r_3^2} \frac{\partial^2 H}{\partial r_1 \partial r_3} \right. \\ \left. + \frac{2(r_1 \cos \theta - r_2)}{r_3^2} \frac{\partial^2 H}{\partial r_2 \partial r_3} - \frac{2}{r_3} \frac{\partial^2 H}{\partial r_3^2} - \frac{2}{r_3^2} \frac{\partial H}{\partial r_3} \right\} + \sin \theta' \cos \phi \left\{ \left(\frac{r_1 r_2 \cos \theta - r_3^2 - r_2^2}{r_1 r_3^3} \right) \sin \theta \frac{\partial H}{\partial r_2} - \frac{2r_2 \sin \theta}{r_1 r_3^2} \frac{\partial H}{\partial r_3} \right\}. \quad (\text{A24}) \end{aligned}$$

Multiplying the scalar product (A24) by $H \cos \theta' \pm \tilde{H} \cos \theta' \cos \theta \mp \tilde{H} \sin \theta' \sin \theta \cos \phi$ and integrating, we have, after substituting for $\cos \theta$ and $\sin \theta$ in terms of r_1 , r_2 , and r_3 , the result

$$\begin{aligned} X = \frac{8\pi^2}{3} \int \left[\left\{ \frac{t_3}{r_1 r_2 r_3} - \frac{r_1 r_2}{r_3^3} + \frac{t_3^2}{4r_1 r_2 r_3^3} \right\} \frac{\partial^2 H}{\partial r_1 \partial r_2} - \frac{t_2}{r_1 r_3^2} \frac{\partial^2 H}{\partial r_1 \partial r_3} - \frac{t_1}{r_2 r_3^2} \frac{\partial^2 H}{\partial r_2 \partial r_3} - \frac{2}{r_3} \frac{\partial^2 H}{\partial r_3^2} - \frac{2}{r_3^2} \frac{\partial H}{\partial r_3} \right] H dV \\ \pm \frac{4\pi^2}{3} \int \left[\left\{ \frac{t_3^2}{r_1^2 r_2^2 r_3} - \frac{t_3}{r_3^3} + \frac{t_3^3}{4r_1^2 r_2^2 r_3^3} \right\} \frac{\partial^2 H}{\partial r_1 \partial r_2} - \frac{t_2 t_3}{r_1^2 r_2 r_3^2} \frac{\partial^2 H}{\partial r_1 \partial r_3} - \frac{t_1 t_3}{r_1 r_2^2 r_3^2} \frac{\partial^2 H}{\partial r_2 \partial r_3} - \frac{2t_3}{r_1 r_2 r_3} \frac{\partial^2 H}{\partial r_3^2} \right. \\ \left. + \left\{ \frac{4r_2}{r_1 r_3^2} - \frac{2t_3}{r_1 r_2 r_3^2} - \frac{t_3^2}{r_1^3 r_2 r_3^2} \right\} \frac{\partial H}{\partial r_3} + \left\{ \frac{2}{r_1 r_3} + \frac{t_1}{r_1 r_3^3} - \frac{t_3^2}{2r_1^3 r_2^2 r_3} - \frac{t_1 t_3^2}{4r_1^3 r_2^2 r_3^3} \right\} \frac{\partial H}{\partial r_2} \right] \tilde{H} dV. \quad (\text{A25}) \end{aligned}$$

If we write $H(r_1, r_2, r_3) = r_1 e^{-\xi r_1 - \eta r_2} M(r_1, r_2, r_3)$, we have finally

$$\begin{aligned} X = \frac{2\pi^2}{3} \int [(r_3)^{-2} \{ r_1^2 M_{12} - \eta r_1^2 M_{11} + (r_1 - \xi r_1^2) M_{21} + (\xi \eta r_1^2 - \eta r_1) M \} \{ (2r_1^2 r_3^2 + 2r_2^2 r_3^2 - 3r_3^4 + r_1^4 + r_2^4 - 2r_1^2 r_2^2) M \} \\ - 4r_1 (r_3)^{-1} M \{ r_1 r_2 t_2 M_{13} + r_1^2 t_1 M_{23} + 2r_1^2 r_2 r_3 M_{33} + (r_2 r_3^2 + 3r_1^2 r_2 - r_2^3 - \xi r_1 r_2 t_2 - \eta r_1^2 t_1) M_{31} \}] e^{-2\xi r_1 - 2\eta r_2} d r_1 d r_2 d r_3 \\ \pm \frac{\pi^2}{3} \int [(r_3)^{-2} \{ M_{12} - \eta M_{11} - \xi M_{21} + \xi \eta M \} \\ \times \{ (r_1^4 r_3^2 + r_2^4 r_3^2 + 3r_3^6 + 6r_1^2 r_2^2 r_3^2 - 5r_1^2 r_3^4 - 5r_2^2 r_3^4 + r_1^6 - r_1^4 r_2^2 - r_1^2 r_2^4 + r_2^6) \tilde{M} \} \\ + 4(r_3)^{-1} \{ -2r_1 r_2 r_3 t_2 M_{33} - r_2 t_2 t_3 M_{13} - r_1 t_1 t_3 M_{23} + (\xi r_2 t_2 t_3 + \eta r_1 t_1 t_3 + 4r_1 r_2 r_3^2 - 4r_1^3 r_2) M_{31} \} \tilde{M} \\ + 2(r_3)^{-2} \{ \eta M - M_{21} \} \{ (2r_1^3 r_3^2 - r_1 r_3^4 - 6r_1 r_2^2 r_3^2 - r_1^5 + 2r_1^3 r_2^2 - r_1 r_2^4) \tilde{M} \}] e^{-(\xi+\eta)(r_1+r_2)} d r_1 d r_2 d r_3. \quad (\text{A26}) \end{aligned}$$

IV. The Spin-Dependent Operators H_3 and H_5

In the case of a singlet state, the total spin S is zero, hence the expectation value of H_3 is zero. Since $\langle \mathbf{s}_1 \cdot \mathbf{s}_2 \rangle = -\frac{3}{4}$, the expectation value of the first term in H_5 is just $2\pi\alpha^2 \langle \delta(\mathbf{r}_3) \rangle$. Also, it can easily be shown that

$$\left\langle \frac{(\mathbf{s}_1 \cdot \mathbf{r}_3)(\mathbf{s}_2 \cdot \mathbf{r}_3)}{r_3^5} \right\rangle = -\frac{1}{4} \left\langle \frac{1}{r_3^3} \right\rangle, \quad (\text{A27})$$

so that the expectation value of the remainder of H_5 is zero. Thus, for a singlet state, the expectation value of $H_3 + H_5$ is equal to $2\pi\alpha^2 \langle \delta(\mathbf{r}_3) \rangle$.

Breit³ has solved the secular equation and determined the expectation values of H_3 and H_5 for 3P states in order to determine their fine structure splitting. For the $J=0$, $J=1$ and $J=2$ levels, the expectation values of H_3 are $-2C$, $-C$, and C , respectively, where

$$C = \frac{1}{4}\alpha^2 [ZC_Z - 3C_e] \quad (\text{A28})$$

in atomic units, and

$$\begin{aligned} C_Z = \frac{8\pi^2}{3} \int \frac{1}{r_1^3} \left[2F(F - \tilde{F} \cos \theta) + \sin \theta \left(F \frac{\partial \tilde{F}}{\partial \theta} - \tilde{F} \frac{\partial F}{\partial \theta} \right) \right] dV, \\ C_e = -\frac{8\pi^2}{3} \int \frac{1}{r_3^3} \left[2F(F - \tilde{F} \cos \theta) + r_1 \sin^2 \theta \left(F \frac{\partial \tilde{F}}{\partial r_2} - \tilde{F} \frac{\partial F}{\partial r_2} \right) \right. \\ \left. + \frac{r_2}{r_1} \left\{ (1 + \cos^2 \theta) F \tilde{F} - 2F^2 \cos \theta + \sin \theta \cos \theta \left(\tilde{F} \frac{\partial F}{\partial \theta} - F \frac{\partial \tilde{F}}{\partial \theta} \right) \right\} \right] dV. \quad (\text{A29}) \end{aligned}$$

We have introduced the extra factor $8\pi^2/3$ into Breit's formula because of a difference in the choice of normalization. Breit uses the function $\psi = (3/8\pi^2)^{1/2}(F \cos\theta_1 - \tilde{F} \cos\theta_2)$, for which $\int (F^2 + \tilde{F}^2 - 2F\tilde{F} \cos\theta) dV = 1$, whereas we have used $\psi = F \cos\theta_1 - \tilde{F} \cos\theta_2$, for which this integral is equal to $3/8\pi^2$.

We now consider H_5 . For a triplet state, $\langle \delta(\mathbf{r}_3) \rangle$ is zero. The expectation value of $\mathbf{s}_1 \cdot \mathbf{s}_2$ is equal to $\frac{1}{4}$ for all values of J , so that

$$\alpha^2 \left\langle \frac{\mathbf{s}_1 \cdot \mathbf{s}_2}{r_3^3} \right\rangle = \frac{\alpha^2}{4} \left\langle \frac{1}{r_3^3} \right\rangle.$$

There remains the term $-3(\mathbf{s}_1 \cdot \mathbf{r}_3)(\mathbf{s}_2 \cdot \mathbf{r}_3)/r_3^5$ in H_5 . Breit has shown that the expectation value of this operator for the $J=0$, $J=1$ and $J=2$ levels is equal to $D' - 3D$, $D' + 2D$ and D' respectively, where the integrals D and D' are

$$D = -\frac{2\pi^2\alpha^2}{5} \int (r_3)^{-5} \{ [4r_1^2 + (6 \cos^2\theta - 2)r_2^2 - 8r_1r_2 \cos\theta] F^2 + [(6 + 2 \cos^2\theta)r_1r_2 - 8r_1^2 \cos\theta] F\tilde{F} \} dV$$

and

$$D' = -\frac{2\pi^2\alpha^2}{5} \int (r_3)^{-5} \{ [2r_1^2 + (4 - 2 \cos^2\theta)r_2^2 - 4r_1r_2 \cos\theta] F^2 + [(6 \cos^2\theta - 2)r_1r_2 - 4r_1^2 \cos\theta] F\tilde{F} \} dV. \quad (\text{A30})$$

Since

$$\left\langle \frac{1}{r_3^3} \right\rangle = \frac{8\pi^2}{3} \int \frac{1}{r_3^3} (2F^2 - 2F\tilde{F} \cos\theta) dV, \quad (\text{A31})$$

it may easily be shown that

$$D' + \frac{1}{2}\alpha^2 \langle 1/r_3^3 \rangle = -\frac{1}{3}D, \quad (\text{A32})$$

so that the expectation value of H_5 is equal to $-10D/3$, $5D/3$ and $-D/3$ for the $J=0$, $J=1$, and $J=2$ levels, respectively.

Thus, finally we have that

$$\begin{aligned} \langle H_3 + H_5 \rangle &= -2C - 10D/3, \quad \text{for } J=0, \\ &= -C + 5D/3, \quad \text{for } J=1, \\ &= C - D/3, \quad \text{for } J=2. \end{aligned} \quad (\text{A33})$$

If we write $F(r_1, r_2, \theta) = r_1 e^{-\xi r_1 - \eta r_2} M(r_1, r_2, r_3)$, the formulas (A29) and (A30) may be written

$$C_Z = \frac{16\pi^2}{3} \int r_2 r_3 M^2 e^{-2\xi r_1 - 2\eta r_2} dr_1 dr_2 dr_3 + \frac{2\pi^2}{3} \int (r_1 r_2)^{-2} \tilde{M} \{ (4r_1^5 r_2^2 - 4r_1^2 r_2^5 - r_1^3 t_3^2 + r_2^3 t_3^2) M_3 - (2r_1^3 r_3 t_3 + 2r_2^3 r_3 t_3) M \} e^{-(\xi+\eta)(r_1+r_2)} dr_1 dr_2 dr_3,$$

$$C_e = \frac{8\pi^2}{3} \int (r_3)^{-2} (r_1^3 r_2 - r_1 r_2^3 + r_1 r_2 r_3^2) M^2 e^{-2\xi r_1 - 2\eta r_2} dr_1 dr_2 dr_3 + \frac{2\pi^2}{3} \int (r_1 r_2 r_3^3)^{-1} \tilde{M} \{ (4r_1^2 r_2^2 r_3^3 + 4\eta r_1^4 r_2^3 r_3 - \eta r_1 r_2^2 r_3 t_3^2 - 4\xi r_1^4 r_2^3 r_3 + \xi r_1 r_2^2 r_3 t_3^2) M + (4r_1^3 r_2^4 r_3 - r_1 r_2^2 r_3 t_3^2) M_1 + (r_1^2 r_2 r_3 t_3^2 - 4r_1^4 r_2^3 r_3) M_2 \} e^{-(\xi+\eta)(r_1+r_2)} dr_1 dr_2 dr_3$$

and

$$D = -\frac{\pi^2\alpha^2}{5} \int (r_3)^{-4} (3r_1^5 r_2 + 3r_1 r_2^5 - 6r_1^3 r_2^3 + 2r_1^3 r_2 r_3^2 - 6r_1 r_2^3 r_3^2 + 3r_1 r_2 r_3^4) M^2 e^{-2\xi r_1 - 2\eta r_2} dr_1 dr_2 dr_3 - \frac{\pi^2\alpha^2}{5} \int (r_3)^{-4} (-3r_1^5 r_2 - 3r_1 r_2^5 + 6r_1^3 r_2^3 + 4r_1^3 r_2 r_3^2 + r_1 r_2 r_3^4) M \tilde{M} e^{-(\xi+\eta)(r_1+r_2)} dr_1 dr_2 dr_3. \quad (\text{A34})$$

APPENDIX B: CALCULATION OF THE THREE-DIMENSIONAL INTEGRALS IN THE (r_1, r_2, ρ) SCHEME

As explained in Sec. III, after integrating over the angular variables, we are left with the evaluation of three-dimensional integrals over the variables (r_1, r_2, r_3) or (r_1, r_2, ρ) . We shall list below the formulas developed for evaluating the (r_1, r_2, ρ) integrals, as they might be of some interest. Their derivation will be outlined in a forthcoming publication.

The integrals are evaluated with the aid of certain auxiliary quantities which are computed by means of the following recurrence relations, all of which are stable when used in the manner indicated.

$$\begin{aligned}
 K(p, q) &= \frac{p}{\lambda} K(p-1, q) + \frac{(p+q)!}{\lambda(\lambda+\mu)^{p+q+1}}, & p, q \geq 0. \\
 H(p, q) &= \frac{q}{\mu} H(p, q-1) + \frac{(p+q)!}{\mu(\lambda+\mu)^{p+q+1}}, & p, q \geq 0. \\
 N(a, b, c) &= -N(a, b-1, c) + \frac{c}{\mu} N(a, b, c-1) + [1+(-1)^{c+1}] \frac{(a+b+c)!}{\mu(\lambda+\mu)^{a+b+c+1}}, & a, b, c \geq 0. \\
 L(a, b+1, c) &= 2L(a+1, b, c) + L(a, b, c+1), & a, b, c \geq 0. \\
 L(a, 0, c) &= \frac{a!c!}{(a+c)!(\lambda+2\mu)^{a+c+1}} \sum_{i=0}^{\infty} \binom{c+i}{i} \frac{1}{(a+c+i+1)} \left(\frac{\lambda+\mu}{\lambda+2\mu}\right)^i, & a, c \geq 0. \\
 O(a+1, b, c) &= \frac{1}{2}[O(a, b+1, c) + O(a, b, c+1)], & a, b, c \geq 0. \\
 O(0, b, c) &= \frac{b!c!}{(b+c)!(\lambda+\mu)^{c+1}(\frac{1}{2}\lambda+\mu)^b} \sum_{i=0}^{b-1} \binom{c+i}{i} \frac{1}{(b-i)} \left(\frac{\frac{1}{2}\lambda+\mu}{\lambda+\mu}\right)^i, & b, c \geq 0. \\
 M_1(a, b+1, c) &= 2M_1(a+1, b, c) + M_1(a, b, c+1), & a, b, c \geq 0. \\
 M_1(a, 0, c) &= \frac{a!c!}{(a+c+1)!\mu^{c+1}(\lambda+2\mu)^{a+1}}, & a, c \geq 0. \\
 M_2(a+1, b, c) &= \frac{1}{2}[M_2(a, b+1, c) + M_2(a, b, c+1)], & a, b, c \geq 0. \\
 M_2(0, b, c) &= \frac{b!c!}{2!(b+c+1)!(\lambda+\mu)^{c+1}(\frac{1}{2}\lambda+\mu)^{b+1}} \sum_{i=0}^b \binom{c+i}{i} \left(\frac{\frac{1}{2}\lambda+\mu}{\lambda+\mu}\right)^i, & b, c \geq 0.
 \end{aligned}
 \tag{B1}$$

The formulas for the integrals are then as follows:

$$\begin{aligned}
 J_0(a, b, c) &\equiv \int_0^\infty r_1^a e^{-\lambda r_1} dr_1 \int_0^\infty r_2^b e^{-\mu r_2} dr_2 \int_{|r_1-r_2|}^{r_2} \rho^c d\rho \\
 &= \frac{1}{(c+1)} N(a, b, c+1) + \frac{[1+(-1)^c]}{c+1} K(a, b+c+1), \quad a, b, c \geq 0 \tag{B2}
 \end{aligned}$$

and for the case $b = -1$,

$$J_0(a, -1, c) = \frac{1}{(c+1)} F(a, c) + \frac{[1+(-1)^c]}{c+1} K(a, c), \quad a, c \geq 0, \tag{B3}$$

where

$$\begin{aligned}
 F(a, c) &= \frac{(a+c+1)!}{\mu^{a+c+2}} \sum_{i=0}^{\infty} \binom{a+c+i+1}{i} \frac{(-\lambda/\mu)^i}{(a+i+1)} \frac{a!(c+1)!}{2^{a+1}\mu^{a+c+2}} \sum_{i=0}^{\infty} \binom{a+i}{i} \frac{(-\lambda/2\mu)^i}{(a+c+2+i)} \\
 &\quad + \frac{(-1)^c(a+c+1)!}{2^{a+1}(\frac{1}{2}\lambda+\mu)^{a+c+2}} \sum_{i=0}^{\infty} \binom{a+c+i+1}{i} \left\{ \sum_{j=0}^a \binom{a}{j} \frac{1}{(c+i+j+2)} \right\} \left(\frac{-\lambda}{\lambda+2\mu}\right)^i.
 \end{aligned}$$

$$\begin{aligned}
J_1(a, b, c) \equiv & \int_0^\infty r_1^a e^{-\lambda r_1} dr_1 \int_0^\infty r_2^b e^{-\mu r_2} dr_2 \int_{|r_1-r_2|-r_1}^{r_2} \frac{\rho^c d\rho}{(\rho+r_1)^\mu} = -J_1(a, b-1, c) \\
& + \frac{a!(b+c)!}{\mu^{a+b+c+2}} \sum_{i=0}^\infty \frac{\binom{a+i}{i}}{(a+b+c+1+i)} \left(\frac{\mu-\lambda}{\mu}\right)^i + (-1)^c \left\{ \frac{a!(b+c)!}{\mu \lambda^a (\lambda+\mu)^{b+c+1}} \sum_{i=0}^{a-1} \binom{b+c+i}{i} \frac{1}{(a-i)} \left(\frac{\lambda}{\lambda+\mu}\right)^i \right\} \\
& - \frac{(a+b+c)!}{\mu} \left\{ L(a, b, c) + (-1)^c O(a, b, c) + \frac{(-1)^c}{(\lambda+\mu)^{a+b+c+1}} \ln\left(\frac{\lambda}{2\mu+\lambda}\right) \right\}, \quad (B4)
\end{aligned}$$

$$\begin{aligned}
J_2(a, b, c) \equiv & \int_0^\infty r_1^a e^{-\lambda r_1} dr_1 \int_0^\infty r_2^b e^{-\mu r_2} dr_2 \int_{|r_1-r_2|-r_1}^{r_2} \frac{\rho^c (r_1^2 - r_2^2) d\rho}{(\rho+r_1)^2} = c[J_1(a+2, b, c-1) - J_1(a, b+2, c-1)] \\
& - M(a+1, b, c) - M(a, b+1, c) + H(a, b+c+1) - H(a+1, b+c) + \begin{cases} 2K(a, b+c+1), & c \text{ even} \\ -2K(a+1, b+c), & c \text{ odd,} \end{cases} \quad (B5)
\end{aligned}$$

where $M(a, b, c) = (a+b+c+1)! [M_1(a, b, c) + (-1)^c M_2(a, b, c)]$.

Inverse powers of r_3 greater than two appear only in the computation of the fine structure integral D , and it is convenient in this case to define the following integral:

$$\begin{aligned}
J_D(a, b, c) \equiv & \int_0^\infty r_1^a e^{-\lambda r_1} dr_1 \int_0^\infty r_2^b e^{-\mu r_2} dr_2 \int_{|r_1-r_2|-r_1}^{r_2} \rho^c d\rho \left\{ \frac{3(r_1^2 - r_2^2)^2}{(\rho+r_1)^4} + \frac{2(r_1^2 - 3r_2^2)}{(\rho+r_1)^2} \right\} \\
= & \frac{c(c-1)}{2} [J_2(a+2, b, c-2) - J_2(a, b+2, c-2)] + 2c [J_1(a+2, b, c-1) - 3J_1(a, b+2, c-1)] \\
& + 3N(a+1, b, c) + 5N(a, b+1, c) - \frac{1}{2}cN(a+2, b, c-1) - cN(a+1, b+1, c-1) - \frac{1}{2}cN(a, b+2, c-1) \\
& + \begin{cases} (2c-6)(a+1)!(b+c)!/\lambda^{a+2}\mu^{b+c+1}, & c \text{ odd} \\ -cK(a+2, b+c-1) + (2c-6)H(a+1, b+c) + (10-c)K(a, b+c+1), & c \text{ even.} \end{cases} \quad (B6)
\end{aligned}$$