# Variational Calculations of Energy and Fine Structure for the 2 $^3P$ State of Helium*

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Using an 18-parameter Hylleraas-type wave function containing only positive powers, a calculation has been carried out for the 2 $^3P$ state of helium by the Ritz variational principle. Breit's reduction was used to convert the problem from six to three variables. The energy was minimized by the approximate solution of an eigenvalue problem. With this wave function the fine structure splitting was calculated. Our best wave function yields an energy 15.5 cm$^{-1}$ above the experimental value while the corresponding fine structure splitting is in error by about 1 part in 10$^2$. All computation was carried out on an IBM-650 computer.

## I. INTRODUCTION

VERY accurate calculations of the energies of the $1s^2\,^1S$ and $1s2s\,^3S$ states of helium have been made recently.[1-3] It is now possible to consider the contributions of relativistic and electrodynamic effects to the observed ionization energies in a meaningful way. These small effects must still be added to the large calculated nonrelativistic energy, however, before a comparison with experiment can be made.

In the $^3P$ states, the spin-dependent part of the theoretical electromagnetic interaction of the two electrons can be compared directly with observed fine-structure splittings. Recent improvements in the experimental accuracy of the fine-structure measurements,[4,5] particularly the direct observation of the splittings as radio-frequency transitions, have made such a comparison possible to an order of accuracy including higher order electrodynamic corrections to the usual fine-structure formulas.

The standard fine-structure expression is of order $\alpha^2$ ry. The recent study by Sucher[6] of the two-electron interaction by the use of the Bethe-Salpeter equation verified the usual $\alpha^2$ ry formulas and showed that the only spin-dependent term of order $\alpha^3$ ry is the expected $\alpha/2\pi$ Schwinger correction to the electron-spin moment. A calculation of the fine structure in a $^3P$ state, accurate to one part in a thousand, would reveal the correctness of the theoretical fine-structure expression to order $\alpha^3$ ry.

The success of our calculations[2] of the energy and electron-charge density at the nucleus with a 12-term Hylleraas wave function for the $^3S$ state encouraged us to attempt a calculation of the nonrelativistic energy and the fine structure of the $1s2p\,^3P$ state of helium. We limit ourselves to wave functions of moderate complexity, i.e., up to 18 terms, which can be handled on an IBM-650 computer.

[1] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).
[2] J. Traub and H. M. Foley, Phys. Rev. **111**, 1098 (1958).
[3] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[4] Brouchard, Chabbel, Chantrel, and Jacquinot, J. phys. radium **13**, 433 (1952).
[5] W. E. Lamb, Phys. Rev. **105**, 559 (1957).
[6] J. Sucher, Phys. Rev **109**, 1010 (1958).

## II. THE WAVE FUNCTION AND THE NONRELATIVISTIC ENERGY

### A. Mathematical Background

Because the potential energy depends only on the three interparticle distances, the operation of rotation in space of the triangle of the three particles commutes with the nonrelativistic Hamiltonian. Therefore, the dependence of the wave function on the Euler angles is determined completely by the angular momentum, symmetry, and parity, and the Schrödinger equation reduces to an equation in three "internal variables." Breit[7] showed that the variational form of this equation for the $1s2p\,^3P$ state is

$$\delta\int\Bigg\{\sum_{i=1,2}\Bigg[\left(\frac{\partial F_1}{\partial r_i}\right)^2-2\cos\theta\frac{\partial F_1}{\partial r_i}\frac{\partial F_2}{\partial r_i}+\left(\frac{\partial F_2}{\partial r_i}\right)^2\Bigg]$$
$$+\frac{2F_1^2}{r_1^2}+\frac{2F_2^2}{r_2^2}+\frac{2\sin\theta}{r_1^2}\frac{\partial F_2}{\partial\theta}F_1+\frac{2\sin\theta}{r_2^2}\frac{\partial F_1}{\partial\theta}F_2$$
$$+\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\Bigg[\left(\frac{\partial F_1}{\partial\theta}\right)^2-2\cos\theta\frac{\partial F_1}{\partial\theta}\frac{\partial F_2}{\partial\theta}+\left(\frac{\partial F_2}{\partial\theta}\right)^2\Bigg]$$
$$+\frac{8m\pi^2}{h^2}(V-E)[F_1^2-2F_1F_2\cos\theta+F_2^2]\Bigg\}d\tau=0 \quad (1)$$

with the normalization condition

$$\int(F_1^2-2F_1F_2\cos\theta+F_2^2)d\tau=1, \quad (2)$$

where $V$ is the potential energy, $E$ is the energy, and

$$d\tau=r_1^2r_2^2\sin\theta dr_1dr_2d\theta. \quad (3)$$

Here $r_1$ and $r_2$ measure the distance from the fixed nucleus to the electrons and $\theta$ is the included angle. The functions $F_1$ and $F_2$ are related by the equation

$$F_1(r_1,r_2,\theta)=F_2(r_2,r_1,\theta). \quad (4)$$

We replaced Breit's variables by the Hylleraas coordinates $s$, $t$, $u$ defined by

$$s=r_1+r_2,$$
$$t=-r_1+r_2, \quad (5)$$
$$u=r_{12},$$

[7] G. Breit, Phys. Rev. **35**, 569 (1930).

where $r_{12}$ is the inter-electronic distance. In these variables the volume element becomes

$$d\tau = \tfrac{1}{8}u(s^2 - t^2)dsdtdu, \qquad (6)$$

where the numerical factor will be suppressed throughout. Equation (4) now becomes

$$F_1(s,t,u) = F_2(s, -t, u). \qquad (7)$$

Triangle inequalities imply $-u \leq t \leq u \leq s \leq \infty$, but symmetry considerations show that we can restrict $t$ to positive values and double the volume element.

After introducing atomic units, the variational equation becomes

$$2\lambda = (M - L)/N, \qquad (8)$$

where $M$ is the expectation value of the kinetic energy, $L$ is the negative of the expectation value of the potential energy, and $N$ is the normalization factor. We employ $\lambda$ to indicate a variable which takes on the value of the energy $E$ for the correct wave function. For example,

$$N = \int_0^\infty ds \int_0^s du \int_0^u dt$$
$$\times [u(s^2 - t^2)(F_1^2 + F_2^2) - 2u(s^2 + t^2 - 2u^2)F_1F_2], \qquad (9)$$

with analogous but more complicated expressions for $L$ and $M$.

To determine the form of our trial functions we note that the hydrogenic approximation for $F_1$ is

$$F_1 = r_1 e^{-\frac{1}{2}Z_a r_1} e^{-Z_i r_2}, \qquad (10)$$

where $Z_a$ is the effective nuclear charge for the outer electron and $Z_i$ is the effective nuclear charge for the inner electron. In Hylleraas variables this becomes

$$F_1 = \tfrac{1}{2}(s - t)e^{-\frac{1}{2}\kappa s}e^{-\frac{1}{2}\kappa\sigma t}, \qquad (11)$$

where

$$\kappa = \tfrac{1}{2}Z_a + Z_i, \quad \kappa\sigma = -\tfrac{1}{2}Z_a + Z_i. \qquad (12)$$

We choose as our trial functions the generalizations

$$F_1(s,t,u) = \psi(\kappa s, \kappa t, \kappa u), \qquad (13)$$

where

$$\psi(s,t,u) = (s - t)e^{-\frac{1}{2}s}e^{-\frac{1}{2}\sigma t}\sum_{i=1}^n c_i\psi_i(s,t,u),$$

and

$$\psi_i(s,t,u) = s^{p_i}t^{q_i}u^{r_i}$$

for $p_i, q_i, r_i \geq 0$ integers. Note that there are two non-linear parameters and $n$ linear parameters to be adjusted. Preliminary estimates of $\sigma$ and $\kappa$ can be derived from Breit's[8] values of $Z_a$ and $Z_i$ and turn out to be

$$\sigma = 0.57, \quad \kappa = 2.535.$$

With this choice of trial function, an upper bound on the energy is given by

$$\lambda = (\kappa^2 M - \kappa L)/N, \qquad (14)$$

where $M, L, N$ are quadratic forms in the $c_i$ with matrix elements depending on $\sigma$ only. We define matrix elements associated with these quadratic forms by

$$L \equiv \sum_{i,j=1}^n c_i c_j L_{ij},$$

$$M \equiv \sum_{i,j=1}^n c_i c_j M_{ij}, \qquad (15)$$

$$N \equiv \sum_{i,j=1}^n c_i c_j N_{ij}.$$

## B. Calculation of $L$, $M$, $N$

All the integrals which appear in this paper are special cases of

$$B(p,q,r,m,\omega) = \int_0^\infty ds \int_0^s du \int_0^u dt \frac{e^{-s}e^{\omega t}s^p t^q u^r}{(s^2 - t^2)^m}. \qquad (16)$$

We are interested in values of these integrals for $m \geq 0$, $r \geq -4$, $p, q \geq 0$, $\omega = \pm\sigma, 0$. Formulas are given in Appendix A. To calculate $L$, $M$, and $N$ we need the integrals given by (A1) and (A5) in Appendix A. Formulas were developed and the computer programmed so that by specifying trial functions and the value of $\sigma$, matrix elements were automatically computed.

Let

$$B(p_i + p_j + n_p, q_i + q_j + n_q, r_i + r_j + n_r, m, \omega)$$
$$\equiv b_{ij}(n_p, n_q, n_r, m, \omega). \qquad (17)$$

Then

$$N_{ij} = b_{ij}(4,0,1,0,-\sigma) - 2b_{ij}(3,1,1,0,-\sigma) + 2b_{ij}(1,3,1,0,-\sigma) - b_{ij}(0,4,1,0,-\sigma)$$
$$+ (-1)^{q_i+q_j}[b_{ij}(4,0,1,0,\sigma) + 2b_{ij}(3,1,1,0,\sigma) - 2b_{ij}(1,3,1,0,\sigma) - b_{ij}(0,4,1,0,\sigma)]$$
$$+ [(-1)^{q_i} + (-1)^{q_j}][-b_{ij}(4,0,1,0,0) + 2b_{ij}(2,0,3,0,0) + b_{ij}(0,4,1,0,0) - 2b_{ij}(0,2,3,0,0)], \qquad (18)$$

$$L_{ij} = -2b_{ij}(4,0,0,0,-\sigma) + 4b_{ij}(3,1,0,0,-\sigma) + 16b_{ij}(3,0,1,0,-\sigma) - 32b_{ij}(2,1,1,0,-\sigma)$$
$$-4b_{ij}(1,3,0,0,-\sigma) + 16b_{ij}(1,2,1,0,-\sigma) + 2b_{ij}(0,4,0,0,-\sigma)$$
$$+ (-1)^{q_i+q_j}[-2b_{ij}(4,0,0,0,\sigma) - 4b_{ij}(3,1,0,0,\sigma) + 16b_{ij}(3,0,1,0,\sigma) + 32b_{ij}(2,1,1,0,\sigma)$$
$$+ 4b_{ij}(1,3,0,0,\sigma) + 16b_{ij}(1,2,1,0,\sigma) + 2b_{ij}(0,4,0,0,\sigma)]$$
$$+ [(-1)^{q_i} + (-1)^{q_j}][2b_{ij}(4,0,0,0,0) - 16b_{ij}(3,0,1,0,0) - 4b_{ij}(2,0,2,0,0) - 16b_{ij}(1,2,1,0,0)$$
$$+ 32b_{ij}(1,0,3,0,0) - 2b_{ij}(0,4,0,0,0) + 4b_{ij}(0,2,2,0,0)], \qquad (19)$$

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press, Inc., New York, 1957), pp. 158–159.

TABLE I. Coefficients for the best 18-parameter function.

| $i$ | $\psi_i = s^{p_i}t^{q_i}u^{r_i}$ | $10^{p_i+q_i+r_i}c_i$ |
|---|---|---|
| 1 | 1 | 1.0000000 |
| 2 | $s$ | 0.3682329 |
| 3 | $t$ | 0.8558912 |
| 4 | $u$ | 0.4964114 |
| 5 | $su$ | 0.7912829 |
| 6 | $tu$ | 0.9620734 |
| 7 | $u^2$ | −0.2614946 |
| 8 | $s^2$ | −0.3473277 |
| 9 | $t^2$ | 0.6345387 |
| 10 | $st$ | −0.3849701 |
| 11 | $su^2$ | 1.0557676 |
| 12 | $tu^2$ | −0.4373243 |
| 13 | $u^3$ | −0.5114887 |
| 14 | $s^2u$ | −0.8403471 |
| 15 | $t^2u$ | 0.0955936 |
| 16 | $stu$ | 0.4888556 |
| 17 | $s^3$ | 0.3829940 |
| 18 | $t^3$ | 0.1349609 |

$\kappa = 2.97$
$\sigma = 0.55$
$\lambda = -2.1331015$ atomic units[a]
$N = 1.3419249 \times 10^5$

[a] The "atomic units" employed in this paper correspond to $Ry_{He}$.

with an analogous but far more complicated formula for $M_{ij}$ with coefficients depending on the trial functions and $\sigma$.

## C. Minimization

We have to minimize

$$\lambda = (\kappa^2 M - \kappa L)/N, \qquad (20)$$

which is a function of $\sigma$ which enters in the matrix elements, $\kappa$ which appears explicitly, and the $n$ parameters $c_i$ which occur in the quadratic forms $L$, $M$, $N$.

In our earlier paper[2] a descent and extrapolation method was employed to minimize $\lambda$. In early stages of the present project, an improved version of that method involving automatic-machine extrapolation was used. For eighteen parameters, however, the machine's memory was not large enough to use this method, and the method described below was employed.

The condition $\partial\lambda/\partial c_i = 0$ implies

$$\sum_{j=1}^{n} (\kappa^2 M_{ij} - \kappa L_{ij} - \lambda N_{ij})c_j = 0, \quad i = 1, 2, \cdots, n. \qquad (21)$$

Let $\sigma$ be considered fixed in the following discussion. Choose $c_n = -1$. Insert trial values of $\lambda = \lambda_0$ and $\kappa = \kappa_0$. Remove the last equation to arrive at a nonhomogeneous system of $n-1$ equations in $n-1$ unknowns. Letting $D_{ij} = \kappa^2 M_{ij} - \kappa L_{ij} - \lambda N_{ij}$, the system may be written as

$$\sum_{j=1}^{n} D_{ij}c_j = 0, \quad i = 1, 2, \cdots, n-1. \qquad (22)$$

This system of equations is then solved.

Consider now the normalized solution

$$(1, v_2/v_1, \cdots, -1/v_1) \equiv (c_1, c_2, \cdots, c_n).$$

If $\lambda_0$ is an eigenvalue of the system of algebraic equations, the last equation of the original set is also satisfied and we have

$$\sum_{j=1}^{n} D_{ij}c_j = 0, \quad i = 1, \cdots, n. \qquad (23)$$

If $\lambda_0$ is not the eigenvalue, then

$$\sum_{j=1}^{n} D_{ij}c_j = \delta_{in}r_n, \qquad (24)$$

where $\delta_{in}$ is the Kronecker symbol and where the residual $r_n$ is a measure of the error in our approximate eigen value. Keeping $\kappa$ fixed and varying $\lambda$, we can make $r_n$ as small as desired. In practice, the second choice of $\lambda$ can be used to reverse the sign of $r_n$ and then the $\lambda$ chosen by interpolation on $r_n$ is usually the desired $\lambda$ for a fixed $\kappa$.

We now vary $\kappa$ and repeat the process till we have $\kappa$ and $\lambda$ chosen so as to minimize (20). This enables us to find the best energy for a given $\sigma$. Finally $\sigma$ is varied and $\kappa$ and $\lambda$ are determined for each value of $\sigma$. When we are finished we will have minimized $\lambda$ as a function of our $n+2$ parameters.

To verify that we are indeed approaching a minimum, $\nabla\lambda$ is calculated and compared with the zero vector. To convince ourselves that there was no significant round-off error, some of the calculations were carried out entirely with double-precision arithmetic. We found that this did not affect the energy value.

It is important that $\sigma$ be varied as few times as possible. Each time that $\sigma$ is varied our integrals and matrix elements must be recalculated. This costs some thirty hours of machine time.

Table I gives coefficients for the best 18-parameter function while Table II gives 2- and 4-parameter coefficients useful for check-out purposes to anyone repeating this investigation.

## III. CALCULATION OF FINE-STRUCTURE SPLITTING

The wave functions obtained above were employed to calculate the expectation values of the fine-structure operators, which are the operators $H_3$ and $H_5$ of Eq. (39.14) in reference 8. The arrangement of the levels and notation for the transitions is shown in Fig. 1.

TABLE II. Coefficients for small number of parameters.

| $i$ | $\psi_i = s^{p_i}t^{q_i}u^{r_i}$ | $10^{p_i+q_i+r_i}c_i$ | |
|---|---|---|---|
| | | 2 parameters | 4 parameters |
| 1 | 1 | 1.00000000 | 1.00000000 |
| 2 | $s$ | 0.00328923 | −0.0471447 |
| 3 | $t$ | | 0.1169497 |
| 4 | $u$ | | 0.1837811 |
| $\sigma$ | | 0.57 | 0.57 |
| $\kappa$ | | 2.55 | 2.57 |
| $\lambda$ | | −2.131072 a.u. | −2.131776 a.u. |
| $N$ | | 6.025406×10⁴ | 5.845328×10⁴ |

The relative positions and of the levels are governed by the two quantities $C$ and $D$ according to the relations

$$\Delta\nu_{02} = -3[C+D],$$

$$\Delta\nu_{12} = -2[C-D], \qquad (25)$$

$$\Delta\nu_{01} = \Delta\nu_{02} - \Delta\nu_{12},$$

and which Breit[9] showed are given, for this state, by

$$C \equiv \left[\frac{eh}{4\pi mc}\right]^2 \gamma, \qquad (26)$$

in which

$$\gamma = z \int \left[ \left[\frac{F_1{}^2}{r_1{}^3} + \frac{F_2{}^2}{r_2{}^3} - \left(\frac{1}{r_1{}^3} + \frac{1}{r_2{}^3}\right)F_1 F_2 \cos\theta \right. \right.$$

$$+ \frac{1}{2}\left(\frac{1}{r_2{}^3} - \frac{1}{r_1{}^3}\right)\left(F_2\frac{\partial F_1}{\partial\theta} - F_1\frac{\partial F_2}{\partial\theta}\right)\sin\theta \Bigg] d\tau$$

$$- 3\int \frac{1}{u^3}\Bigg[ F_1{}^2 + F_2{}^2 - 2F_1 F_2 \cos\theta + \frac{r_1}{r_2}F_2(F_1 - F_2 \cos\theta)$$

$$+ \frac{r_2}{r_1}F_1(F_2 - F_1 \cos\theta) + \tfrac{1}{2}\sin^2\theta \Bigg\{ r_2\left(F_2\frac{\partial F_1}{\partial r_1} - F_1\frac{\partial F_2}{\partial r_1}\right)$$

$$- r_1\left(F_2\frac{\partial F_1}{\partial r_2} - F_1\frac{\partial F_2}{\partial r_2}\right) + \left(\frac{r_2}{r_1} - \frac{r_1}{r_2}\right)\left(F_2\frac{\partial F_1}{\partial\theta} - F_1\frac{\partial F_2}{\partial\theta}\right)$$

$$\left. \left. \times\cot\theta - \left(\frac{r_2}{r_1} + \frac{r_1}{r_2}\right)F_1 F_2 \right\}\Bigg] d\tau, \qquad (27)$$

$$D \equiv -\frac{3}{5}\left[\frac{eh}{4\pi mc}\right]^2 \delta, \qquad (28)$$
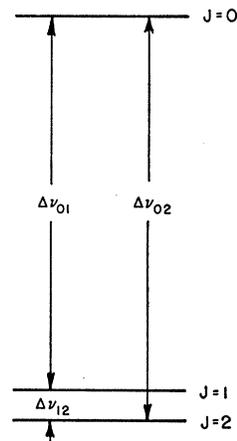


FIG. 1. Schematic energy-level splitting in $2\,{}^3P$ helium (reference 8, p. 188).

$$\delta = \int \frac{1}{u^5}[2(a\alpha + b\beta)^2 - (a\beta - \alpha b)^2]d\tau, \qquad (29)$$

where $a = F_1 - F_2 \cos\theta$, $b = F_2 \sin\theta$, $\alpha = r_1 - r_2 \cos\theta$, and $\beta = r_2 \sin\theta$.

In Hylleraas variables and with the present wave functions, we must calculate

$$C = (\kappa^3/N)(\alpha^2/2)R_{He}\gamma, \qquad (30)$$

$$D = -\tfrac{3}{5}(\kappa^3/N)(\alpha^2/2)R_{He}\delta, \qquad (31)$$

where $\alpha$ is the fine-structure constant, and $\gamma$ and $\delta$ are quadratic forms with matrix elements defined by

$$\gamma \equiv \sum_{i,j=1}^{n} c_i c_j \gamma_{ij},$$

$$\delta \equiv \sum_{i,j=1}^{n} c_i c_j \delta_{ij}. \qquad (32)$$

$$\gamma_{ij} = 6b_{ij}(3,1,-2,0,-\sigma) - 6b_{ij}(2,0,0,0,-\sigma) - 6b_{ij}(1,3,-2,0,-\sigma) + 16b_{ij}(1,0,1,0,-\sigma)$$

$$+ 6b_{ij}(0,2,0,0,-\sigma) + 16b_{ij}(0,1,1,0,-\sigma)$$

$$+ [(-1)^{q_i} + (-1)^{q_j}][-6b_{ij}(2,0,0,0,0) + 6b_{ij}(0,2,0,0,0)]$$

$$+ (-1)^{q_i+q_j}[-6b_{ij}(3,1,-2,0,\sigma) - 6b_{ij}(2,0,0,0,\sigma) + 6b_{ij}(1,3,-2,0,\sigma) + 16b_{ij}(1,0,1,0,\sigma)$$

$$+ 6b_{ij}(0,2,0,0,\sigma) - 16b_{ij}(0,1,1,0,\sigma)]$$

$$+ [(-1)^{q_i} + (-1)^{q_j}][3\sigma b_{ij}(5,2,-2,1,0) - 3\sigma b_{ij}(5,0,0,1,0) - 3\sigma b_{ij}(3,4,-2,1,0) + 3\sigma b_{ij}(3,0,2,1,0)$$

$$+ 3\sigma b_{ij}(1,4,0,1,0) - 3\sigma b_{ij}(1,2,2,1,0)]$$

$$+ [(-1)^{q_i} - (-1)^{q_j}][3(q_i - q_j)b_{ij}(5,1,-2,1,0) - 3(q_i - q_j)b_{ij}(5,-1,0,1,0)$$

$$- 3(p_i - p_j + q_i - q_j)b_{ij}(3,3,-2,1,0) + 3(p_i - p_j)b_{ij}(3,1,0,1,0)$$

$$+ 3(q_i - q_j)b_{ij}(3,-1,2,1,0) + 3(p_i - p_j)b_{ij}(1,5,-2,1,0) + 3(q_i - q_j)b_{ij}(1,3,0,1,0)$$

$$- 3(p_i - p_j + q_i - q_j)b_{ij}(1,1,2,1,0) - 3(p_i - p_j)b_{ij}(-1,5,0,1,0) + 3(p_i - p_j)b_{ij}(-1,3,2,1,0)]$$

$$+ [(-1)^{q_i} + (-1)^{q_j}][-16b_{ij}(5,0,1,2,0) - 64b_{ij}(3,2,1,2,0)$$

$$+ 32b_{ij}(3,0,3,2,0) - 48b_{ij}(1,4,1,2,0) + 96b_{ij}(1,2,3,2,0)]$$

$$+ [(-1)^{q_i} - (-1)^{q_j}][r_i - r_j][-24b_{ij}(4,3,-1,2,0) + 24b_{ij}(4,1,1,2,0) + 32b_{ij}(2,3,1,2,0) - 24b_{ij}(2,1,3,2,0)$$

$$- 8b_{ij}(2,5,-1,2,0) + 8b_{ij}(0,5,1,2,0) - 8b_{ij}(0,3,3,2,0)]. \qquad (33)$$

[9] G. Breit, Phys. Rev. 36, 385 (1930).

$$\delta_{ij} = 3b_{ij}(4,2,-4,0,-\sigma) - b_{ij}(4,0,-2,0,-\sigma) - 4b_{ij}(3,1,-2,0,-\sigma) - 3b_{ij}(2,4,-4,0,-\sigma)$$
$$+ 3b_{ij}(2,0,0,0,-\sigma) + 4b_{ij}(1,3,-2,0,-\sigma) + b_{ij}(0,4,-2,0,-\sigma) - 3b_{ij}(0,2,0,0,-\sigma)$$
$$+ (-1)^{q_i+q_j}[3b_{ij}(4,2,-4,0,\sigma) - b_{ij}(4,0,-2,0,\sigma) + 4b_{ij}(3,1,-2,0,\sigma) - 3b_{ij}(2,4,-4,0,\sigma)$$
$$+ 3b_{ij}(2,0,0,0,\sigma) - 4b_{ij}(1,3,-2,0,\sigma) + b_{ij}(0,4,-2,0,\sigma) - 3b_{ij}(0,2,0,0,\sigma)]$$
$$+ [(-1)^{q_i} + (-1)^{q_j}][-3b_{ij}(4,2,-4,0,0) + b_{ij}(4,0,-2,0,0) + 3b_{ij}(2,4,-4,0,0) + b_{ij}(2,0,0,0,0)$$
$$- b_{ij}(0,4,-2,0,0) - b_{ij}(0,2,0,0,0)]. \quad (34)$$

For the calculation of $C$, the integrals that occur are given by (A1), (A4), (A5), (A6), (A7), (A8). For the calculation of $D$, (A1), (A2), (A3), (A4) are required.

Note that $C$ contains (A8) which has a singularity of form $\lim_{t\to 0+} E_i(t)$ and that $D$ contains (A2) which has a singularity of form $\lim_{t\to 0+} \ln t$. One can verify that whenever these formulas appear in our calculations, the structure of the matrix formulas and integral formulas are such that the singularities cancel out identically. In the numerical work, these singularities are therefore ignored.

### IV. RESULTS AND DISCUSSION

The nonrelativistic energies for various numbers of parameters are shown in Table IV. Although the energy is rather sensitive to the value of $\sigma$ for a wave function of very few parameters, Table III, there is virtually no

TABLE III. Dependence of energy on $\sigma$ for small number of parameters. Energy entries are in atomic units. $(s-t)e^{-\frac{1}{2}s}e^{-\frac{1}{2}\sigma t}$ has been suppressed from wave functions.

| $\sigma \backslash F_1$ | $c_1$ | $c_1 + c_4 u$ | $c_1 + c_2 s + c_3 t + c_4 u$ |
|---|---|---|---|
| 0.55 | −2.1303 | −2.1317 | −2.1318 |
| 0.57 | −2.1307 | −2.1313 | −2.1318 |
| 0.59 | −2.1303 | −2.1305 | −2.1317 |

TABLE IV. Summary of nonrelativistic energy calculations.

| No. of parameters | Energy in a.u. | Difference with experiment in cm$^{-1}$ | Calculated by |
|---|---|---|---|
| 2 | −2.1308 | 520.5 | Breit |
| 4 | −2.131831 | 294.3 | Authors |
| 7 | −2.132519 | 143.3 | Authors |
| 10 | −2.132820 | 77.2 | Authors |
| 14 | −2.132971 | 44.1 | Authors |
| 18 | −2.133102 | 15.5 | Authors |
|  | −2.133172 | 0.0 | Experimental |

dependence for a larger number of parameters and therefore the comparisons in Table IV are made with a fixed value $\sigma = 0.55$. From Table IV, it is clear that the convergence of the energy toward a limiting value, with increasing number of parameters, is very slow. For the $1s2s \, ^3S$ state it was evident, already with 12 parameters, that one was within a very few wave numbers of a limiting energy value. In the present work, however, at the 18-parameter stage we calculate an energy which is still 15.5 cm$^{-1}$ above the experimental value. The relativistic and "mass polarization" terms which are estimated to contribute less than 5 cm$^{-1}$ are not included in Table IV.

The slow convergence of the energy value and the still sizeable gap between calculated and observed energies at 18 parameters must be considered disappointing. No systematic study was made of the degree of sensitivity of the energy to various kinds of terms in the wave function. Quite possibly a different choice of trial functions would have yielded a better energy for the same number of parameters.

The fine structure has been the principal subject of interest in this calculation. Results for various numbers of parameters and those of previous calculations are shown in Table V. Since $\Delta\nu_{12}$ is the difference between two nearly equal calculated terms, the comparison with experiment is probably most meaningful for the quantities $C$ and $D$ defined above. It will be noted that an increase in the number of parameters brings the calculated values of $C$ and $D$ steadily closer to the experimental values. For our best wave function, the discrepancy is about one percent, which is substantially greater than the experimental error. We note that the "error" in our nonrelativistic energy is about 40 parts in $10^6$. From the usual estimate of accuracy of a variational wave function we can expect the value of an

TABLE V. Summary of calculations of fine structure.

| No. of parameters | Energy in a.u. | $\Delta\nu_{02}$ | $\Delta\nu_{12}$ | $\Delta\nu_{01}$ | $C$ | $D$ | Calculated by |
|---|---|---|---|---|---|---|---|
|  |  | 1.01 | 0.07 | 0.94 | −0.186 | −0.151 | Araki[a] |
| 2 | −2.1308 | 1.119 | 0.142 | 0.977 | −0.222 | −0.151 | Breit[b] |
| 4 | −2.131831 | 1.09249 | 0.125056 | 0.967434 | −0.213345 | −0.150817 | Authors |
| 7 | −2.132519 | 1.08664 | 0.108248 | 0.978392 | −0.208169 | −0.154045 | Authors |
| 10 | −2.132820 | 1.08921 | 0.101958 | 0.987252 | −0.207025 | −0.156046 | Authors |
| 14 | −2.132971 | 1.06946 | 0.088114 | 0.981348 | −0.200271 | −0.156214 | Authors |
| 18 | −2.133102 | 1.06855 | 0.083352 | 0.985198 | −0.198930 | −0.157254 | Authors |
|  | −2.133172 | 1.0645 | 0.0765 | 0.988 | −0.1965 | −0.1583 | Experimental[c,d] |

[a] G. Araki, Proc. Phys. Math. Soc. (Japan) 19, 128 (1937).
[b] See reference 9.
[c] See reference 4.
[d] I. Wieder and W. E. Lamb, Phys. Rev. 107, 125 (1957). This paper reports a very accurate measurement of $\Delta\nu_{12}$. Their result is $\Delta\nu_{12} = 0.076443$. Since this was the only splitting reported, $C$ and $D$ could not be calculated.

operator such as the fine structure to be no better than about 7 parts in $10^3$ which is approximately the accuracy achieved.

The degree of agreement with the experimental fine structure found in the present work is sufficient to verify the $\alpha^2$ ry terms but is not precise enough to determine any discrepancy in the $\alpha^3$ ry terms. A wave function accurate enough for this purpose would presumably yield a nonrelativistic energy within about one part per million of the true energy.

### ACKNOWLEDGMENTS

### APPENDIX A

In this Appendix we give formulas for the integrals which appear in this paper. All integrals are of the type

$$B(p,q,r,m,\omega) \equiv \int_0^\infty ds \int_0^s du \int_0^u dt \frac{e^{-s}e^{\omega t}s^p t^q u^r}{(s^2-t^2)^m}.$$

We need consider only the cases $p \geq 0$, $q \geq 0$, $m \geq 0$, $r \geq -4$, $\omega = \pm \sigma, 0$.

The following functions appear in the formulas.

$$\mathrm{Ei}(t) \equiv \int_t^\infty \frac{e^{-x}}{x} dx, \quad 0 < t < \infty.$$

Note that

$$\lim_{t \to 0+} \mathrm{Ei}(t) = \infty.$$

$$Y(\beta,n) \equiv \int_0^\infty e^{\beta t} t^n \,\mathrm{Ei}(t) dt, \quad \beta < 1, \ n = \text{integer}.$$

For $\beta \neq 0$,

$$Y(\beta,n) = \frac{n!}{\beta^{n+1}}\bigg[(-1)^{n+1}\ln(1-\beta)$$
$$+(-1)^n \sum_{i=1}^n (-1)^i \left(\frac{\beta}{1-\beta}\right)^i \frac{1}{i}\bigg].$$

$$Y(0,n) = n!/(n+1).$$

We list the integrals which are needed. Let

$$\nu = p+q+r+2.$$

#### (1) Integrals of Type $m=0$

For $r \neq -1$, $p+r+1 \geq 0$, $q+r+1 \geq 0$:

$$B(p,q,r,0,\omega)$$
$$= \frac{1}{r+1}\bigg\{(p+r+1)! \sum_{j=0}^{p+r+1} \frac{(\nu-1-j)!}{(p+r+1-j)!}\left(\frac{1}{1-\omega}\right)^{\nu-j}$$
$$-p! \sum_{j=0}^p \frac{(\nu-1-j)!}{(p-j)!}\left(\frac{1}{1-\omega}\right)^{\nu-j}\bigg\}. \quad \text{(A1)}$$

For $r \neq -1$, $q+r+1 = -1$, $p+r+1 \geq 0$:

$$B(p,q,r,0,\omega)$$
$$= \frac{1}{r+1}\bigg\{(p+r+1)! \sum_{j=0}^{p+r+1} \frac{(\nu-1-j)!}{(p+r+1-j)!}\left(\frac{1}{1-\omega}\right)^{\nu-j}$$
$$-p! \sum_{j=0}^{p-1} \frac{(\nu-1-j)!}{(p-j)!}\left(\frac{1}{1-\omega}\right)^{\nu-j} -p! \lim_{t\to 0+}\mathrm{Ei}(t)\bigg\}. \quad \text{(A2)}$$

For $r \neq -1$, $p+r+1 = -1$, $q+r+1 \geq 0$:

$$B(p,q,r,0,\omega)$$
$$= \frac{1}{r+1}\bigg\{Y(\omega,\nu) - p! \sum_{j=0}^p \frac{(\nu-1-j)!}{(p-j)!}\left(\frac{1}{1-\omega}\right)^{\nu-j}\bigg\}, \quad \text{(A3)}$$

$$B(p,q,-1,0,\omega)$$
$$= p!\bigg\{\sum_{j=0}^{p-1}\sum_{k=0}^j \frac{(q+k)!}{k!(j+1)}\left(\frac{1}{1-\omega}\right)^{q+k+1} + Y(\omega,q)\bigg\}. \quad \text{(A4)}$$

#### (2) Integrals of Type $m=1$

For $r \geq 0$:

$$B(p,q,r,1,0) = \frac{(p+q+r)!}{r+1}\bigg\{(-1)^q \frac{\ln 2}{2}[1+(-1)^r]$$
$$+ \sum_{\substack{k=1 \\ (k\ \mathrm{odd})}}^{q+r} \frac{1}{q+r+1-k} - \sum_{\substack{k=1 \\ (k\ \mathrm{odd})}}^{q-1} \frac{1}{q-k}\bigg\}. \quad \text{(A5)}$$

For $p+q \geq 2$:

$$B(p,q,-2,1,0)$$
$$= (p+q-2)!(-1)^{q+1}\bigg\{\ln 2 + \sum_{j=1}^{q-1} \frac{(-1)^j}{j}\bigg\}. \quad \text{(A6)}$$

For $p+q-1 \geq 0$:

$$B(p,q,-1,1,0) = (p+q-1)!\bigg\{\frac{\pi^2}{12}[1+\tfrac{1}{2}(-1)^q]$$
$$- \tfrac{1}{2}\sum_{\beta=2}^q [1+(-1)^{q+\beta}]\left(\frac{1}{\beta-1}\right)^2\bigg\}. \quad \text{(A7)}$$

#### (3) Integrals of Type $m=2$

For $p+q+r-2 \geq 0$, $r \geq 0$:

$$B(p,q,r,2,0) = \frac{(p+q+r-2)!}{r+1}\bigg\{-\left(\frac{r+1}{4}\right)\lim_{t\to 0+}\ln t$$
$$-\tfrac{1}{4}(-1)^q[q-1+(-1)^r(q+r)]\ln 2$$
$$+\tfrac{1}{8}(-1)^q[1+(-1)^r]+\tfrac{1}{2}\sum_{\substack{j=1 \\ (j\ \mathrm{odd})}}^{q-3} \frac{j+1}{q-j-2}$$
$$-\tfrac{1}{2}\sum_{k=1}^{q+r-2} \frac{k+1}{q+r+1-k}\bigg\}. \quad \text{(A8)}$$