Variational Calculations of the 2 ³S State of Helium*

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(Received March 13, 1958)

With a 12-parameter Hylleraas-type wave function containing only positive powers, a new calculation has been carried out for the 2 ³S state of helium by the Ritz variational principle. The energy was minimized by a descent process. A nonrelativistic energy of -1.0876088 Hylleraas units was reached as compared with the best previously published value of -1.0876015 Hylleraas units from a 6-parameter function. When mass-polarization and $\alpha^2 R_y$ corrections are included, the 12-parameter function gives an ionization potential 2.52 cm^{-1} less than the experimental value of 38 454.64 cm^{-1}. The electron density at the nucleus is also calculated and compared with the experimental hyperfine-spectrum value. All numerical work was carried out on an I.B.M. 650 computer.

I. INTRODUCTION

A LONG series of calculations have been made of the energy of the ground state of helium,[1] culminating in the 38-parameter calculation of Kinoshita.[2] When relativistic and mass-polarization corrections are made, the resulting comparison with the experimental values of the ionization energy must be considered as very satisfactory.

The six-parameter variational calculations of Hylleraas[3] and Huang[4] represent the most accurate previously published wave functions of the 2 ³S state.[5] They differ from the ground-state function with respect to symmetry and also in that two different exponential functions must be included, corresponding to 1s and 2s orbits. No calculation of the relativistic corrections has hitherto been made for the 2 ³S state. The mass-polarization term was calculated by Stone[6] with a six-parameter function.

In this paper are presented the results of a twelve-parameter variational calculation of the 2 ³S nonrelativistic energy together with relativistic and mass-polarization corrections. Compared with the elaborate character of the wave functions employed in some recent work,[2,7] the 12-parameter function employed here may be regarded as of intermediate complexity. In spite of this fact the total energy seems to converge very well, and indeed the agreement of our calculated value with experiment seems to be as good as was obtained by Chandrasekhar and Herzberg[8] for the ground state with an 18-parameter function. This is undoubtedly related to the fact that the independent-particle hydrogenic wave function, to which the Hylleraas trial function with few parameters reduces, is a much better approximation for a state with one electron excited than it is for the ground state with both electrons in the same orbit. (See also the discussion of mass polarization below.)

An additional quantity of interest which can be compared with experiment is the total charge density at the nucleus which enters as a factor in the hyperfine interaction.[9]

The rather lengthy calculations of the relativistic corrections have not previously been done for the excited states. It has appeared worthwhile to give an account of the methods employed in these calculations.

II. NONRELATIVISTIC INFINITE NUCLEAR MASS PROBLEM

A. Mathematical Preliminaries

The nonrelativistic Schrödinger equation for the helium atom is

$$\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)\psi+\left(E+\frac{Ze^2}{r_1}+\frac{Ze^2}{r_2}-\frac{e^2}{r_{12}}\right)\psi=0, \quad (1)$$

* Work supported by the National Science Foundation.
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[1] H. A. Bethe and E. E. Salpeter, *Handbook of Physics* (Academic Press, Inc., New York, 1957), Vol. 35, Atoms I, pp. 204–278.
[2] T. Kinoshita, Phys. Rev. 105, 1490 (1957).
[3] E. Hylleraas, Z. Physik 54, 347 (1929); 65, 209 (1930).
[4] Su-chu Huang, Astrophys. J. 108, 354 (1948).
[5] Hylleraas gave 0.08761×4R_{He}'hc for the nonrelativistic ionization potential of the 2 ³S state of helium. This calculation was in error and was later corrected by Hylleraas[6] to 0.0876015×4R_{He}'hc. Huang employed a wave function which is formally identical with that of Hylleraas but obtained a value of 0.087600×4R_{He}'hc due, it must be supposed, to incomplete minimization.
[6] A. P. Stone, Proc. Phys. Soc. (London) A68, 1152 (1955).
[7] Tycko, Thomas, and King, Phys. Rev. 109, 369 (1958).

[8] S. Chandrasekhar and G. Herzberg, Phys. Rev. 98, 1050 (1955).
[9] W. B. Teutsch and V. W. Hughes, Phys. Rev. 103, 1461 (1954).

where r_1 and r_2 are the radial coordinates of the electrons with the fixed nucleus as origin and r_{12} is the interelectronic distance. We choose the following units

$$a_0/4=1; \quad 4Rch=1, \quad (2)$$

where a_0 is the radius of the first Bohr orbit and R is the "Rydberg for infinite mass." (2) fixes the units of length and implies

$$\hbar^2/8m=1; \quad e^2=2. \quad (3)$$

For this choice of units, (1) becomes

$$(\nabla_1^2+\nabla_2^2)\psi+\left(\frac{E}{4}+\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{2r_{12}}\right)\psi=0. \quad (4)$$

The following "elliptic coordinates" are introduced:

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

The Schrödinger equation becomes

$$\psi_{ss}+\psi_{tt}+\psi_{uu}+\frac{4s}{s^2-t^2}\psi_s-\frac{4t}{s^2-t^2}\psi_t+\frac{2}{u}\psi_u$$
$$+\frac{2s(u^2-t^2)}{u(s^2-t^2)}\psi_{us}+\frac{2t(s^2-u^2)}{u(s^2-t^2)}\psi_{ut}$$
$$+\left(\frac{E}{8}+\frac{2s}{s^2-t^2}-\frac{1}{4u}\right)\psi=0, \quad (6)$$

where the subscripts indicate differentiation.

Following Hylleraas we replace (6) by the variational formulation

$$\lambda=(M-L)/N, \quad (7)$$

where

$$M=\int_0^\infty ds\int_0^s du\int_0^u dt[u(s^2-t^2)(\psi_s^2+\psi_t^2+\psi_u^2)$$
$$+2s(u^2-t^2)\psi_s\psi_u+2t(s^2-u^2)\psi_t\psi_u], \quad (8)$$

$$L=\int_0^\infty ds\int_0^s du\int_0^u dt[2su-\tfrac{1}{4}(s^2-t^2)]\psi^2, \quad (9)$$

$$N=\tfrac{1}{8}\int_0^\infty ds\int_0^s du\int_0^u dt\,\psi^2 u(s^2-t^2). \quad (10)$$

The limits of integration come from the following considerations. Triangle inequalities imply $-u\leqslant t\leqslant u\leqslant s\leqslant\infty$. Since the integrands in (8), (9), (10) are even functions of t, we can restrict t to positive values and double the volume element.

We choose as trial functions

$$\psi=\sum_{i=1}^n c_i\varphi_i(s,t,u).$$

Let

$$\varphi_i(s,t,u)\equiv\psi_i(\kappa s,\kappa t,\kappa u).$$

Let

$$\psi_i(s,t,u)=e^{-\frac{1}{2}\sigma s}s^{p_i}t^{q_i}u^{r_i}f_i(\tfrac{1}{2}\sigma t), \quad (11)$$

where

$$f_i(\tfrac{1}{2}\sigma t)=\left\{\begin{array}{c}\sinh(\tfrac{1}{2}\sigma t)\\\cosh(\tfrac{1}{2}\sigma t)\end{array}\right\}.$$

We note that there are two nonlinear parameters σ, κ, while for the ground state only one such parameter is used. Our trial function is a generalization of an antisymmetrized product of two hydrogen-like wave functions.

Equation (7) becomes

$$\lambda=(\kappa^2 M-\kappa L)/N. \quad (12)$$

M, L, N become quadratic forms in the c_i, for our choice of ψ, with matrix coefficients functions of σ only.

$$M\equiv\sum_{i,j=1}^n c_ic_jM_{ij}(\sigma),$$

$$L\equiv\sum_{i,j=1}^n c_ic_jL_{ij}(\sigma), \quad (13)$$

$$N\equiv\sum_{i,j=1}^n c_ic_jN_{ij}(\sigma).$$

In series (11) we restricted ourselves to p_i, q_i, $r_i\geqslant 0$. It has been pointed out[10] that such a series cannot satisfy the Schrödinger equation formally. Kinoshita removed this restriction, replacing it by the requirement that his function obey Kato's boundary conditions.[11] The question as to how closely a series with our restriction can approximate an eigenfunction has not been decided. Since we achieved a very definite improvement over the six-parameter result, we have limited ourselves to positive powers in this investigation. It should be pointed out that introduction of negative powers would complicate formulas for the matrix elements, but would otherwise cause no new difficulties.

To calculate the expectation values of the various operators encountered in this paper, three types of integrals were needed. To establish notation we list them all below:

$$U(p,q,r,d)=\int_0^\infty ds\int_0^s du\int_0^u dt\,e^{-\sigma s}s^p t^q u^r$$
$$\times\left\{\begin{array}{c}\sinh^2(\tfrac{1}{2}\sigma t)\\\sinh(\tfrac{1}{2}\sigma t)\cosh(\tfrac{1}{2}\sigma t)\\\cosh^2(\tfrac{1}{2}\sigma t)\end{array}\right\}, \quad (14)$$

[10] Bartlett, Gibbons, and Dunn, Phys. Rev. 47, 679 (1935).
[11] T. Kato, Trans. Am. Math. Soc. 70, 195, 212 (1951); Commun. Pure Appl. Math. 10, No. 2, 151 (1957).

when $p \geqslant 0, q \geqslant 0, r \geqslant -2$,

$$V(p,q,r,d) = \int_0^\infty ds \int_0^s du \int_0^u dt \, e^{-s} \frac{s^p t^q u^r}{s+t}$$

$$\times \left\{ \begin{array}{l} \sinh^2(\tfrac{1}{2}\sigma t) \\ \sinh(\tfrac{1}{2}\sigma t)\cosh(\tfrac{1}{2}\sigma t) \\ \cosh^2(\tfrac{1}{2}\sigma t) \end{array} \right\}, \quad (15)$$

when $p \geqslant 0, q \geqslant 0, r \geqslant -1$,

$$W(p,q,r,d) = \int_0^\infty ds \int_0^s du \int_0^u dt \, e^{-s} \frac{s^p t^q u^r}{s-t}$$

$$\times \left\{ \begin{array}{l} \sinh^2(\tfrac{1}{2}\sigma t) \\ \sinh(\tfrac{1}{2}\sigma t)\cosh(\tfrac{1}{2}\sigma t) \\ \cosh^2(\tfrac{1}{2}\sigma t) \end{array} \right\}, \quad (16)$$

when $p \geqslant 0, q \geqslant 0, r \geqslant -1$,

where

$d=1$ corresponds to $\sinh^2(\tfrac{1}{2}\sigma t)$,

$d=0$ corresponds to $\sinh(\tfrac{1}{2}\sigma t)\cosh(\tfrac{1}{2}\sigma t)$,

$d=-1$ corresponds to $\cosh^2(\tfrac{1}{2}\sigma t)$.

B. Calculation of L, M, N

Any of our ψ_i can be represented by a four-tuple of numbers $(p_i, q_i, r_i, \theta_i)$, where

$$\theta_i = \tfrac{1}{2} \quad \text{if} \quad f_i(\tfrac{1}{2}\sigma t) = \sinh(\tfrac{1}{2}\sigma t),$$
$$\theta_i = -\tfrac{1}{2} \quad \text{if} \quad f_i(\tfrac{1}{2}\sigma t) = \cosh(\tfrac{1}{2}\sigma t).$$

Note that multiplication of θ_i by -1 is equivalent to interchange of $\sinh(\tfrac{1}{2}\sigma t)$ and $\cosh(\tfrac{1}{2}\sigma t)$. That is, -1 operating on θ_i is equivalent to $(2/\sigma)(d/dt)$ operating on $f_i(\tfrac{1}{2}\sigma t)$.

TABLE I. Summary of nonrelativistic values.

i	ψ_i	$10^{p_i+q_i+r_i} c_i$	
		6-Par.	12-Par.
1	$(0,0,0,\ \ \tfrac{1}{2})$	1.0000000	1.0000000
2	$(1,0,0,\ \ \tfrac{1}{2})$	−2.9048000	−2.8596935
3	$(0,1,0,-\tfrac{1}{2})$	−2.8390000	−2.7618353
4	$(0,0,1,\ \ \tfrac{1}{2})$	−0.8218000	−0.9133951
5	$(1,0,1,\ \ \tfrac{1}{2})$	−0.6630000	−0.8072628
6	$(0,1,1,-\tfrac{1}{2})$	1.1300000	1.1314343
7	$(0,0,2,\ \ \tfrac{1}{2})$		0.2711045
8	$(1,0,2,\ \ \tfrac{1}{2})$		−0.0019456
9	$(0,1,2,-\tfrac{1}{2})$		−0.0981906
10	$(2,0,0,\ \ \tfrac{1}{2})$		0.3274611
11	$(0,2,0,\ \ \tfrac{1}{2})$		−0.0331554
12	$(1,1,0,-\tfrac{1}{2})$		0.0369968
κ		0.67504	0.66444
σ		0.55000	0.55000
L		304.61561	250.08928
M		225.62677	188.19418
N		94.53310	76.392594
λ		−1.0876015	−1.0876088

Let

$$U(p_i+p_j+a, q_i+q_j+b, r_i+r_j+c, d) = u_{ij}(a,b,c,d), \quad (17)$$

then

$$L_{ij} = 2u_{ij}(1,0,1,\theta_i+\theta_j) + \tfrac{1}{4}[u_{ij}(0,2,0,\theta_i+\theta_j) - u_{ij}(2,0,0,\theta_i+\theta_j)], \quad (18)$$

$$\begin{aligned} M_{ij} =\ & p_i p_j [u_{ij}(0,0,1,\theta_i+\theta_j) \\ & - u_{ij}(-2,2,1,\theta_i+\theta_j)] \\ & - \tfrac{1}{2}(p_i+p_j)[u_{ij}(1,0,1,\theta_i+\theta_j) \\ & - u_{ij}(-1,2,1,\theta_i+\theta_j)] \\ & + \tfrac{1}{4}[u_{ij}(2,0,1,\theta_i+\theta_j) - u_{ij}(0,2,1,\theta_i+\theta_j)] \\ & + q_i q_j [u_{ij}(2,-2,1,\theta_i+\theta_j) \\ & - u_{ij}(0,0,1,\theta_i+\theta_j)] \\ & + \tfrac{1}{2}\sigma q_i [u_{ij}(2,-1,1,\theta_i-\theta_j) \\ & - u_{ij}(0,1,1,\theta_i-\theta_j)] \\ & + \tfrac{1}{2}\sigma q_j [u_{ij}(2,-1,1,-\theta_i+\theta_j) \\ & - u_{ij}(0,1,1,-\theta_i+\theta_j)] \\ & + \tfrac{1}{4}\sigma^2 [u_{ij}(2,0,1,-\theta_i-\theta_j) \\ & - u_{ij}(0,2,1,-\theta_i-\theta_j)] \\ & + r_i r_j [u_{ij}(2,0,-1,\theta_i+\theta_j) \\ & - u_{ij}(0,2,-1,\theta_i+\theta_j)] \\ & + (p_i r_j + p_j r_i)[u_{ij}(0,0,1,\theta_i+\theta_j) \\ & - u_{ij}(0,2,-1,\theta_i+\theta_j)] \\ & - \tfrac{1}{2}(r_i+r_j)[u_{ij}(1,0,1,\theta_i+\theta_j) \\ & - u_{ij}(1,2,-1,\theta_i+\theta_j)] \\ & + (q_i r_j + q_j r_i)[u_{ij}(2,0,-1,\theta_i+\theta_j) \\ & - u_{ij}(0,0,1,\theta_i+\theta_j)] \\ & + \tfrac{1}{2}\sigma r_i [u_{ij}(2,1,-1,\theta_i-\theta_j) \\ & - u_{ij}(0,1,1,\theta_i-\theta_j)] \\ & + \tfrac{1}{2}\sigma r_j [u_{ij}(2,1,-1,-\theta_i\pm\theta_j) \\ & - u_{ij}(0,1,1,-\theta_i+\theta_j)], \quad (19) \end{aligned}$$

$$N_{ij} = \tfrac{1}{8}[u_{ij}(2,0,1,\theta_i+\theta_j) - u_{ij}(0,2,1,\theta_i+\theta_j)]. \quad (20)$$

C. Minimization

Let us consider σ held constant. Then minimize (12) as follows. First we minimize explicitly with respect to κ by the condition $\partial\lambda/\partial\kappa=0$. Thus one parameter is determined by $\kappa=L/2M$ and (12) becomes

$$\lambda = -\tfrac{1}{4}L^2/MN. \quad (21)$$

Equivalently, we maximize

$$f(\sigma_0,\mathbf{c}) = L^2/MN; \quad \mathbf{c} = c_1, \cdots, c_n \quad (22)$$

by an iterative procedure[12]

$$c_i^{l+1} = c_i^l + b \left[\frac{\partial f}{\partial c_i}(\sigma_0,\mathbf{c}^l) \right] \Big/ \left[\frac{\partial^2 f}{\partial c_i^2}(\sigma_0,\mathbf{c}^l) \right];$$

$$i = 1, \cdots, n, \quad (23)$$

[12] This procedure is based on ideas of T. Kinoshita (private communication).

where b is a suitably chosen scalar which will be discussed later. By differentiating (22) we see

$$\frac{\partial f}{\partial c_i} = 2f\left(\frac{2L_i}{L} - \frac{M_i}{M} - \frac{N_i}{N}\right),\qquad(24)$$

$$\frac{\partial^2 f}{\partial c_i^2} = \frac{1}{f}\left(\frac{\partial f}{\partial c_i}\right)^2 + 2f\left[\frac{2}{L^2}(LL_{ii} - 2L_i^2)\right.$$

$$\left. -\frac{1}{M^2}(MM_{ii} - 2M_i^2) - \frac{1}{N^2}(NN_{ii} - 2N_i^2)\right],\quad(25)$$

where

$$L_i = \sum_{j=1}^{n} L_{ij}c_j;\quad M_i = \sum_{j=1}^{n} M_{ij}c_j;\quad N_i = \sum_{j=1}^{n} N_{ij}c_j.$$

By using the same $\partial^2 f/\partial c_i^2$ for a large number of iterations, the machine time per iteration becomes small since only $\partial f/\partial c_i$ need be calculated at each step. After iterating a few hundred times, we extrapolate the c_i for a few hundred iterations and then start iterating again with these new c_i. We choose b so that there is little oscillation in the c_i and $\partial f/\partial c_i$. This descent method has the advantage that round-off error cannot build up.

To minimize the energy with respect to σ, we select a value of σ (from a lower order calculation, for example) and calculate L_{ij}, M_{ij}, N_{ij}. For this value of σ we can determine κ, $\mathbf{c}$, λ by the process discussed above. We repeat this procedure for a number of values of σ. We thus obtain a set of pairs (σ_j, λ_j). By interpolation or extrapolation we can determine the value of σ corresponding to the best value of λ and use this σ to make a final choice of the remaining parameters and of λ.

The numerical values of the wave-function parameters and the energy at minimization for the 6- and 12-parameter functions are listed in Table I.

III. CORRECTION FOR NUCLEAR MOTION AND RELATIVITY

A. Nuclear Motion

In a coordinate system with respect to the center of mass of the atom, the Schrödinger equation becomes[1]

$$\left[-\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) + V - \frac{\hbar^2}{M_{\text{He}}}\nabla_1\cdot\nabla_2\right]\psi = E\psi,\quad(26)$$

where M_{He} is the mass of the helium nucleus and $\mu = mM_{\text{He}}/(m + M_{\text{He}})$.

Motion of the nucleus has modified the Schrödinger equation in two ways.

(1) The actual mass has been replaced by the reduced mass of the electron. This can be dealt with by replacing the Rydberg for infinite nuclear mass R_∞ by $R_\infty(1 - m/M_{\text{He}})$ when we express our energy in wave numbers.

(2) A perturbing term is added which changes the energy by

$$\epsilon = -\frac{\hbar^2}{M_{\text{He}}}\int \psi(\nabla_1\cdot\nabla_2)\psi d\tau.\qquad(27)$$

Integrating by parts and introducing Hylleraas units, we have

$$\epsilon = \frac{8m}{M_{\text{He}}}\int \nabla_1\psi\cdot\nabla_2\psi d\tau,\qquad(28)$$

or for our functions

$$\epsilon = \frac{m\kappa^2}{M_{\text{He}}N}\int \nabla_1\psi\cdot\nabla_2\psi d\tau,\qquad(29)$$

$$P \equiv \int_0^\infty ds \int_0^s du \int_0^u dt\, \nabla_1\psi\cdot\nabla_2\psi u(s^2 - t^2)$$

$$= \int_0^\infty ds \int_0^s du \int_0^u dt[u(s^2 + t^2 - 2u^2)(\psi_s^2 - \psi_t^2)$$

$$- u(s^2 - t^2)\psi_u^2 - 2s(u^2 - t^2)\psi_u\psi_s$$

$$- 2t(s^2 - u^2)\psi_u\psi_t].\quad(30)$$

Note that

$$P = -M + 2\int_0^\infty ds \int_0^s du$$

$$\times \int_0^u dt[u(s^2 - u^2)\psi_s^2 - u(t^2 - u^2)\psi_t^2],\quad(31)$$

where M was defined by (8), and is known for a given value of σ. Therefore we can shorten our calculations considerably by calculating the integral expression on the right side of (31). For our functions

$$R \equiv \sum_{i,j=1}^{n} c_ic_jR_{ij} = P + M,$$

$$R_{ij} = 2p_ip_j[u_{ij}(0,0,1,\theta_i+\theta_j) - u_{ij}(-2,0,3,\theta_i+\theta_j)]$$
$$- (p_i+p_j)[u_{ij}(1,0,1,\theta_i+\theta_j) - u_{ij}(-1,0,3,\theta_i+\theta_j)]$$
$$+ \tfrac{1}{2}[u_{ij}(2,0,1,\theta_i+\theta_j) - u_{ij}(0,0,3,\theta_i+\theta_j)]$$
$$- 2q_iq_j[u_{ij}(0,0,1,\theta_i+\theta_j) - u_{ij}(0,-2,3,\theta_i+\theta_j)]$$
$$- \sigma q_j[u_{ij}(0,1,1,-\theta_i+\theta_j) - u_{ij}(0,-1,3,-\theta_i+\theta_j)]$$
$$- \sigma q_i[u_{ij}(0,1,1,\theta_i-\theta_j) - u_{ij}(0,-1,3,\theta_i-\theta_j)]$$
$$- \tfrac{1}{2}\sigma^2[u_{ij}(0,2,1,-\theta_i-\theta_j) - u_{ij}(0,0,3,-\theta_i-\theta_j)].$$
$$(32)$$

Results of Mass-Polarization Calculations

6-parameter	12-parameter
5.27×10^{-7} Hylleraas units	5.13×10^{-7} Hylleraas units
0.232 cm^{-1}	0.225 cm^{-1}

We note that the mass-polarization term, which is a measure of the electron correlation, is only 1/20 of the value 4.79 cm^{-1} calculated for the ground state.[1] This seems to be a rather striking evidence of the independent character of the motion of the two electrons in this state.

B. Relativistic Corrections

The Breit equation in Pauli approximation in position space is[1]

$$\sum_{i=0}^{6} H_i\psi = E\psi, \tag{33}$$

$$H_0 = V - \frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2). \tag{34}$$

H_0 is the Hamiltonian for the nonrelativistic equation.

$$H_1 = \frac{-\hbar^4}{8m^3c^2}(\nabla_1^4 + \nabla_2^4). \tag{35}$$

H_1 is the relativistic correction due to variation of mass with velocity.

$$H_2 = \frac{e^2\hbar^2}{2(mc)^2}\frac{1}{u}\left(\nabla_1\cdot\nabla_2 + \frac{\mathbf{u}\cdot(\mathbf{u}\cdot\nabla_1)\nabla_2}{u^2}\right). \tag{36}$$

H_2 corresponds to the classical relativistic correction to the electromagnetic interaction between electrons.

$\langle H_3\rangle = 0$ for all S states.

$$H_4 = \frac{e\hbar^2}{(2mc)^2}(\nabla_1\cdot\mathbf{\mathcal{E}}_1 + \nabla_2\cdot\mathbf{\mathcal{E}}_2). \tag{37}$$

H_4 is a relativistic term characteristic of the Dirac theory.

$\langle H_5\rangle = 0$ since it is proportional to $\langle\delta^3(\mathbf{u})\rangle$, and $\langle H_6\rangle = 0$.

(A) Calculation of $\langle H_1\rangle$

$$\langle H_1\rangle = \frac{-\hbar^4}{8m^3c^2}(\langle\nabla_1^4\rangle + \langle\nabla_2^4\rangle), \tag{38}$$

$$\langle\nabla_1^4\rangle = \int\psi\nabla_1^4\psi d\tau. \tag{39}$$

It has been pointed out[13] that using this integral leads to difficulties which can be avoided by using the form $\int(\nabla_1^2\psi)^2 d\tau$,

$$\nabla_1^2\psi(s,t,u) = \psi_{ss} - 2\psi_{st} + \psi_{tt} + \frac{4}{s-t}(\psi_s - \psi_t) + \psi_{uu}$$
$$+ \frac{2}{u}\psi_u + 2\left(\frac{-st+u^2}{u(s-t)}\right)(\psi_{us} - \psi_{ut}), \tag{40}$$

$$\nabla_2^2\psi(s,t,u) = \psi_{ss} + 2\psi_{st} + \psi_{tt} + \frac{4}{s+t}(\psi_s + \psi_t) + \psi_{uu}$$
$$+ \frac{2}{u}\psi_u + 2\left(\frac{st+u^2}{u(s+t)}\right)(\psi_{us} + \psi_{ut}). \tag{41}$$

[13] J. Sucher and H. M. Foley, Phys. Rev. 95, 966 (1954).

Note

$$\nabla_1^2\psi(s, t, u) = -\nabla_2^2\psi(s, -t, u), \tag{42}$$

where the minus sign is due to the antisymmetric character of our wave functions. Since the operators ∇_1^2 and ∇_2^2 are not even functions of t, we cannot restrict ourselves to positive powers of t. Instead we note that

$$\int(\nabla_1^2\psi)^2 d\tau = \int_0^\infty ds\int_0^s du\int_{-u}^u dt(\nabla_1^2\psi)^2 u(s^2-t^2)$$
$$= \int_0^\infty ds\int_0^s du\int_0^u dt(\nabla_1^2\psi)^2 u(s^2-t^2)$$
$$+ \int_0^\infty ds\int_0^s du\int_0^u dt(\nabla_2^2\psi)u(s^2-t^2). \tag{43}$$

With these limits of integration we can make use of the integrals defined in (14)–(16). Note that

$$\langle(\nabla_1^2\psi)^2\rangle = \langle(\nabla_2^2\psi)^2\rangle.$$

We shall carry out in some detail the calculation of the first integral on the right side of (43). The second integral can be done similarly.

If we try to express this integral in terms of U, V, W [(14), (15), (16)] integrals we would arrive at an expression which has on the order of 1000 terms. We show how to avoid such a formula. Let

$$\nabla_1^2\psi = A_1\psi + B_1\psi/(s-t), \tag{44}$$

where

$$A_1\psi \equiv \psi_{ss} - 2\psi_{st} + \psi_{tt} + \psi_{uu} + (2/u)\psi_u, \tag{45}$$

$$B_1\psi \equiv 4(\psi_s - \psi_t) + 2[(-st+u^2)/u](\psi_{us} - \psi_{ut}). \tag{46}$$

Then

$$\int_0^\infty ds\int_0^s du\int_0^u dt(\nabla_1^2\psi)^2 u(s^2-t^2)$$
$$= \int_0^\infty ds\int_0^s du\int_0^u dt(A_1\psi)^2 u(s^2-t^2)$$
$$+ 2\int_0^\infty ds\int_0^s du\int_0^u dt(A_1\psi)(B_1\psi)u(s+t)$$
$$+ \int_0^\infty ds\int_0^s du\int_0^u dt(B_1\psi)^2\frac{u(s+t)}{s-t}. \tag{47}$$

The first two integrals on the right side of (47) require only integrals of type $U(p,q,r,d)$. The last integral requires type $W(p,q,r,d)$. We separate our calculation into three parts because of the limited storage capacity of our machine.

We note again that the ψ_i can be represented by a four-tuple of numbers $(p_i, q_i, r_i, \theta_i)$. Let

$$G_i(a, b, c, \pm\theta_i) \equiv (p_i+a, q_i+b, r_i+c, \pm\theta_i), \quad (48)$$

then

$$
\begin{aligned}
A_1\psi_i = &\tfrac{1}{4}(1+\sigma^2)G_i(0, 0, 0, \theta_i) \\
&+ r_i(r_i+1)G_i(0, 0, -2, \theta_i) \\
&+ q_iG_i(0, -1, 0, \theta_i) \\
&+ q_i(q_i-1)G_i(0, -2, 0, \theta_i) \\
&- p_iG_i(-1, 0, 0, \theta_i) \\
&- 2p_iq_iG_i(-1, -1, 0, \theta_i) \\
&+ p_i(p_i-1)G_i(-2, 0, 0, \theta_i) \\
&+ \tfrac{1}{2}\sigma G_i(0, 0, 0, -\theta_i) \\
&+ \sigma q_iG_i(0, -1, 0, -\theta_i) \\
&\qquad\qquad - \sigma p_iG_i(-1, 0, 0, -\theta_i). \quad (49)
\end{aligned}
$$

$$
\begin{aligned}
B_1\psi_i = &r_iG_i(1, 1, -2, \theta_i) \\
&+ 2r_iq_iG_i(1, 0, -2, \theta_i) \\
&- 2p_ir_iG_i(0, 1, -2, \theta_i) \\
&- (r_i+2)G_i(0, 0, 0, \theta_i) \\
&- (4q_i+2r_iq_i)G_i(0, -1, 0, \theta_i) \\
&+ (4p_i+2p_ir_i)G_i(-1, 0, 0, \theta_i) \\
&- \sigma(r_i+2)G(0, 0, 0, -\theta_i) \\
&\qquad\qquad + \sigma r_iG_i(1, 1, -2, -\theta_i). \quad (50)
\end{aligned}
$$

To illustrate the calculation of (47) we consider in detail

$$\int_0^\infty ds \int_0^s du \int_0^u dt (B_1\psi)^2 \frac{u(s+t)}{s-t} \equiv B_1^2, \quad (51)$$

$$B_1\psi_i = \sum_\beta F_i^\beta(\sigma)G_i(a^\beta, b^\beta, c^\beta, d^\beta\theta_i); \quad (52)$$

where $d^\beta = \pm 1$.

$$B_1^2 \equiv \sum_{i,j=1}^n c_ic_jB_{1ij}^2,$$

where

$$
\begin{aligned}
B_{1ij}^2 = &\int_0^\infty ds \int_0^s du \int_0^u dt (B_1\psi_i)(B_1\psi_j)\frac{u(s+t)}{s-t} \\
= &\sum_{\beta,\gamma} F_i^\beta(\sigma)F_j^\gamma(\sigma) \int_0^\infty ds \int_0^s du \\
&\times \int_0^u dt\, G_i(a^\beta, b^\beta, c^\beta, d^\beta\theta_i)G_j(a^\gamma, b^\gamma, c^\gamma, d^\gamma\theta_j)\frac{u(s+t)}{s-t} \\
= &\sum_{\beta,\gamma} F_i^\beta(\sigma)F_j^\gamma(\sigma) \int_0^\infty ds \int_0^s du \int_0^u dt \\
&\times [G_{ij}(a^\beta+a^\gamma+1, b^\beta+b^\gamma, c^\beta+c^\gamma+1, d^\beta\theta_i+d^\gamma\theta_j) \\
&+ G_{ij}(a^\beta+a^\gamma, b^\beta+b^\gamma+1, c^\beta+c^\gamma+1, d^\beta\theta_i+d^\gamma\theta_j)] \\
&\qquad\qquad\qquad\qquad\qquad\qquad \times \frac{1}{s-t}. \quad (53)
\end{aligned}
$$

In Eq. (53)

$$G_{ij}(a, b, c, d) = (p_i+p_j+a, q_i+q_j+b, r_i+r_j+c, d).$$

Let

$$W(p_i+p_j+a, q_i+q_j+b, r_i+r_j+c, d) = w_{ij}(a, b, c, d), \quad (54)$$

where W was defined by (16). Then

$$
\begin{aligned}
B_{1ij}^2 = \sum_{\beta,\gamma} F_i^\beta(\sigma)F_j^\gamma(\sigma) \\
\times [w_{ij}(a^\beta+a^\gamma+1, b^\beta+b^\gamma, c^\beta+c^\gamma+1, d^\beta\theta_i+d^\gamma\theta_j) \\
+ w_{ij}(a^\beta+a^\gamma, b^\beta+b^\gamma+1, c^\beta+c^\gamma+1, d^\beta\theta_i+d^\gamma\theta_j)].
\end{aligned}
$$

To enable us to calculate these matrix elements, we have to load into the machine the tabulated integrals, the four-tuples $(p_i, q_i, r_i, \theta_i)$ and the four-tuples $G_i(a^\beta, b^\beta, c^\beta, d^\beta)$. The machine can then be programed to form all matrix elements.

Results for $\langle H_1 \rangle$.—

6-parameter	12-parameter
$-5.22976\alpha^2$ Hylleraas units	$-5.22052\alpha^2$ Hylleraas units
-122.225 cm^{-1}	-122.009 cm^{-1}

(B) Calculation of $\langle H_2 \rangle$

$$\langle H_2 \rangle = \frac{e^2\hbar^2}{2(mc)^2} \int \psi \left(\frac{\nabla_1 \cdot \nabla_2}{u} + \frac{\mathbf{u} \cdot (\mathbf{u} \cdot \nabla_1)\nabla_2}{u^3} \right) \psi d\tau. \quad (55)$$

Let x_{ij} be the jth coordinate of the ith electron relative to the nucleus.

$$
\begin{aligned}
&\frac{\nabla_1 \cdot \nabla_2}{u} + \frac{\mathbf{u} \cdot (\mathbf{u} \cdot \nabla_1)\nabla_2}{u^3} \\
&= -\frac{1}{u}\sum_{i=1}^3 \frac{\partial^2}{\partial x_{1i}\partial x_{2i}} + \frac{1}{u^3} \\
&\qquad \times \sum_{i=1}^3 \sum_{k=1}^3 \left[(x_{2i}-x_{1i})(x_{2k}-x_{1k})\frac{\partial^2}{\partial x_{1i}\partial_{2k}} \right], \quad (56)
\end{aligned}
$$

$$
\begin{aligned}
D \equiv &\int \psi \left(\frac{\nabla_1 \cdot \nabla_2}{u} + \frac{\mathbf{u} \cdot (\mathbf{u} \cdot \nabla_1)\nabla_2}{u^3} \right) \psi d\tau \\
= &\frac{1}{8}\int_0^\infty ds \int_0^s du \int_0^u dt\psi \left[\left(s^2+t^2+\frac{s^2t^2}{u^2}-3u^2 \right) \right. \\
&\times (\psi_{ss}-\psi_{tt}) + \frac{4s}{u}(t^2-u^2)\psi_{su} + \frac{4t}{u}(u^2-s^2)\psi_{tu} \\
&\left. -2(s^2-t^2)\psi_{uu} - \frac{2}{u}(s^2-t^2)\psi_u \right], \quad (57)
\end{aligned}
$$

$$D \equiv \frac{1}{8} \sum_{i,j=1}^{n} c_i c_j D_{ij},$$

$$
\begin{aligned}
D_{ij} = &\tfrac{1}{4}(1-\sigma^2)u_{ij}(2,2,-2,\theta_i+\theta_j) \\
&+\tfrac{1}{4}(1-\sigma^2)u_{ij}(2,0,0,\theta_i+\theta_j) \\
&-[2r_j+4r_jq_j+q_j(q_j-1)+2r_j(r_j-1)] \\
&\times u_{ij}(2,0,-2,\theta_i+\theta_j) \\
&-q_j(q_j-1)u_{ij}(2,-2,0,\theta_i+\theta_j) \\
&-(p_j+2r_j)u_{ij}(1,2,-2,\theta_i+\theta_j) \\
&-(p_j-2r_j)u_{ij}(1,0,0,\theta_i+\theta_j) \\
&+\tfrac{1}{4}(1-\sigma^2)u_{ij}(0,2,0,\theta_i+\theta_j) \\
&+[2r_j+4p_jr_j+p_j(p_j-1)+2r_j(r_j-1)] \\
&\times u_{ij}(0,2,-2,\theta_i+\theta_j)-\tfrac{3}{4}(1-\sigma^2)u_{ij}(0,0,2,\theta_i+\theta_j) \\
&+[4r_jq_j-4r_jp_j+p_j(p_j-1)-q_j(q_j-1)] \\
&\times u_{ij}(0,0,0,\theta_i+\theta_j)+3q_j(q_j-1)u_{ij}(0,-2,2,\theta_i+\theta_j) \\
&-p_ju_{ij}(-1,2,0,\theta_i+\theta_j)+3p_ju_{ij}(-1,0,2,\theta_i+\theta_j) \\
&+p_j(p_j-1)u_{ij}(-2,2,0,\theta_i+\theta_j) \\
&-3p_j(p_j-1)u_{ij}(-2,0,2,\theta_i+\theta_j) \\
&-\sigma(q_j+2r_j)u_{ij}(2,1,-2,\theta_i-\theta_j) \\
&-\sigma q_j u_{ij}(2,-1,0,\theta_i-\theta_j) \\
&-\sigma(q_j-2r_j)u_{ij}(0,1,0,\theta_i-\theta_j) \\
&+3\sigma q_j u_{ij}(0,-1,2,\theta_i-\theta_j). \quad (58)
\end{aligned}
$$

Results for $\langle H_2 \rangle$.—

6-parameter	12-parameter
$-8.46\times10^{-4}\alpha^2$	$-7.99\times10^{-4}\alpha^2$
Hylleraas units	Hylleraas units
-1.98×10^{-2} cm^{-1}	-1.87×10^{-2} cm^{-1}

(C) Calculation of $\langle H_4 \rangle$

$$H_4 = \frac{e\hbar^2}{(2mc)^2}(\nabla_1 \cdot \boldsymbol{\mathcal{E}}_1 + \nabla_2 \cdot \boldsymbol{\mathcal{E}}_2), \quad (59)$$

where $\boldsymbol{\mathcal{E}}_i = -\nabla_i V$ is the Coulomb field due to the nucleus plus the other electron.

$$\langle H_4 \rangle = \frac{4\pi e^2 \hbar^2 Z}{(2mc)^2}\langle \delta^3(\mathbf{r}_1) \rangle; \quad (60)$$

where

$$\langle \delta^3(\mathbf{r}_1) \rangle = \frac{\kappa^3}{16\pi^2 N}\int \psi^2(\mathbf{r}_1,0)d\tau_1$$

$$= \frac{\kappa^3}{4\pi N}\int_0^\infty \psi^2(r_1)r_1^2 dr_1. \quad (61)$$

Let

$$Q = \int_0^\infty \psi^2(r_1)r_1^2 dr_1 \equiv \sum_{i,j=1}^n c_i c_j Q_{ij}, \quad (62)$$

$$Q_{ij} = \int_0^\infty \psi_i(r_1)\psi_j(r_1)r_1^2 dr_1, \quad (63)$$

$$\psi_i(r_1) = e^{-\frac{1}{2}r_1}r_1^{p_i+q_i+r_i}f_i(\tfrac{1}{2}\sigma r_1), \quad (64)$$

$$Q_{ij} = \tfrac{1}{4}(p_i+p_j+q_i+q_j+r_i+r_j+2)!$$

$$\times A_{ss,sc,cc}(\sigma, p_i+p_j+q_i+q_j+r_i+r_j+3). \quad (65)$$

(See Appendix A.)

Results for $\langle H_4 \rangle$.—

6-parameter	12-parameter
$4.1481\alpha^2$ Hylleraas units	$4.1435\alpha^2$ Hylleraas units
96.945 cm^{-1}	96.838 cm^{-1}

IV. CALCULATION OF $D(0)$

$$D(0) \equiv 4\pi a_0^3\left[\int_{\tau_1} |\psi(\mathbf{r}_1,0)|^2 d\tau_1 + \int_{\tau_2} |\psi(0,\mathbf{r}_2)|^2 d\tau_2\right], \quad (66)$$

where $\psi(\mathbf{r}_1\mathbf{r}_2)$ is the normalized two-electron wave function and a_0 is the radius of the first Bohr orbit of hydrogen. We summarize our results.

	6-parameter	12-parameter	Experimental[14]
$D(0)$	33.18456	33.14795	33.18388 ± 0.00023

V. RESULTS AND DISCUSSION

It is instructive to compare the results of the present calculations, Table II, with those made for the ground state of helium with various numbers of variational parameters as presented by Kinoshita.[2] Referring to the nonrelativistic energies obtained directly from the variational calculations, we note that the increase in

TABLE II. Summary.[a]

	Six parameters	Twelve parameters
$\alpha^2 = 5.32504 \times 10^{-5}$; $R_{He^4} = 109722.267$ cm^{-1}		
$\langle H_0 \rangle$	-1.0876015 Hyl. units $-477\,336.41$ cm^{-1}	-1.0876088 Hyl. units $-477\,339.61$ cm^{-1}
$\epsilon =$ mass polar.	5.27×10^{-7} Hyl. units 0.232 cm^{-1}	5.13×10^{-7} Hyl. units 0.225 cm^{-1}
$\langle H_1 \rangle$	$-5.22976\alpha^2$ Hyl. units -122.225 cm^{-1}	$-5.22052\alpha^2$ Hyl. units -122.009 cm^{-1}
$\langle H_2 \rangle$	$-8.46 \times 10^{-4}\alpha^2$ Hyl. units -1.98×10^{-2} cm^{-1}	$-7.99 \times 10^{-4}\alpha^2$ Hyl. units -1.87×10^{-2} cm^{-1}
$\langle H_4 \rangle$	$4.1481\alpha^2$ Hyl. units 96.945 cm^{-1}	$4.1435\alpha^2$ Hyl. units 96.838 cm^{-1}
Relativistic shift in ionization energy $=E_i$	$0.08245\alpha^2$ Hyl. units 1.9267 cm^{-1}	$0.07784\alpha^2$ Hyl. units 1.8192 cm^{-1}
$E_i-\epsilon$	1.695 cm^{-1}	1.594 cm^{-1}

	6 parameters	12 parameters	Experimental
Ionization energy	0.0876054 Hyl. units 38 449.05 cm^{-1}	0.0876124 Hyl. units 38 452.12 cm^{-1}	0.0876181 Hyl. units 38 454.64 cm^{-1} [b]
$D(0)$	33.18456	33.14795	33.18388 ± 0.00023

	Six parameters	Twelve parameters
Ionization energy shift (experimental-theoretical)	5.59 cm^{-1}	2.52 cm^{-1}

[a] Constants taken from E. R. Cohen and J. W. M. Dumond: *Handuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 35.
[b] F. Paschen and R. Gotze, *Seriengesetze der Linienspektren* (1922).

[14] R. Novick and E. Commins (private communication).

number of parameters from 6 to 12 in the 2 ^3S calculations resulted in a lowering of the nonrelativistic energy by only 3 cm^{-1}. This is approximately the amount by which the energy was lowered in the ground state work on increasing the number of parameters from 14 to 18. This apparent convergence of the 2 ^3S calculation for a moderate number of parameters is presumably an indication that hydrogenic single-particle wave functions are a much better approximation in excited states than in the ground state. The marked reduction in the electron correlation, measured by the mass-polarization term, as compared with the ground-state value is consistent with this interpretation.

The evaluation of the expectation values of the relativistic and other operators is *a priori* much less accurate than that of the nonrelativistic Hamiltonian by the variational method. The fact that our net relativistic correction differs by only 0.1 cm^{-1} between the 6- and 12-parameter functions is perhaps sufficient justification for the belief that these corrections can be applied, and a comparison of the total energy with the experimental ionization energy can be made which is significant.

We note that the final theoretical value for the ionization energy is only 2.52 cm^{-1} below the present experimental value. This is a very satisfactory result in view of the moderate number of variational parameters employed and is consistent with the remarks in the first paragraph of this section. We note that the greater experimental accuracy for the 2 ^3S state as compared with the ground state, makes it a better state in which to compare theory, including higher order electrodynamic corrections, with experiment.

The comparison of the electron charge density at the nucleus with the experimental value derived from the hyperfine splitting has been discussed by Teutsch and Hughes.[9] The "experimental value" $D(0)$ is derived with neglect of nuclear structure effects. We note that while a six-parameter wave function yields a value of $D(0)$ which agrees almost exactly with the experimental value, the value which we obtain with our 12-parameter function differs by 1 part in 10^3 from the experimental value deduced by Teutsch and Hughes. The following rough argument indicates that no better agreement can really be expected with the wave function available. From the apparent rate of convergence of the variational energy value together with the degree of agreement with the experimental ionization energy one cannot argue that the variational energy (nonrelativistic) is closer than 1 part in 10^6 to the energy of the 2 ^3S state. Because of the minimal property of this energy value, the wave function, on the average, is not better determined that 1 part in 10^3. The observed accuracy of our 12-parameter value of $D(0)$ is consistent with this estimate, and the closer agreement with experiment found with 6-parameters must be regarded as accidental.

APPENDIX A

To evaluate the numerous integrals encountered in this investigation, we define the following functions.

For n an integer:

For $\beta < 1$,

$$Y(\beta,n) = \int_0^\infty e^{\beta t} t^n \, \mathrm{Ei}(t) dt, \tag{A1}$$

where

$$\mathrm{Ei}(t) = \int_t^\infty \frac{e^{-x}}{x} dx.$$

For $\beta \neq 0$,

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

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

Recursion:

For $\beta \neq 0$

$$Y(\beta,n) = -(n/\beta)Y(\beta, n-1) + (1/\beta)\frac{(n-1)!}{(1-\beta)^n}.$$

For n an integer:

For $\beta < 2$,

$$L(\beta,n) = \int_0^\infty e^{\beta t} t^n \, \mathrm{Ei}^2(t) dt. \tag{A2}$$

Recursion:

$$L(\beta,n) = -(n/\beta)L(\beta, n-1) + (2/\beta)Y(\beta-1, n-1),$$

$$L(\beta,0) = \frac{\pi^2}{6\beta} + \frac{2}{\beta}\sum_{j=1}^\infty \frac{(-1)^j}{j^2}(1-\beta)^j.$$

In particular we need

$$L(1.55, 0) = 1.90403182,$$

$$L(0.45, 0) = 1.48382912,$$

$$L(1, 0) \quad = \pi^2/6.$$

$$H(\beta,n) = \int_0^\infty e^{\beta t} t^n dt \int_1^\infty \frac{e^{-xt} \ln x}{x-1} dx. \tag{A3}$$

For $\beta > \tfrac{1}{2}$,

$$H(\beta,n) = \frac{n!}{(1-\beta)^{n+1}}\left[\frac{-(\ln\beta)^2}{2}+\ln\beta\,\ln(1-\beta)\right.$$

$$-\sum_{i=1}^{\infty}\frac{1}{j^2}\left(\frac{\beta-1}{\beta}\right)^i-\ln(1-\beta)\sum_{i=1}^{n}\frac{1}{j}$$

$$\left.\times\left(\frac{\beta-1}{\beta}\right)^i+\sum_{i=2}^{n}\sum_{j=1}^{i-1}\frac{1}{ij}\left(\frac{\beta-1}{\beta}\right)^{i-j}\right].$$

For $\beta < \tfrac{1}{2}$, and $\beta \neq 0$,

$$H(\beta,n) = \frac{n!}{(1-\beta)^{n+1}}\left[\frac{\pi^2}{6}+\tfrac{1}{2}[\ln(1-\beta)]^2\right.$$

$$+\sum_{j=1}^{\infty}\left(\frac{\beta}{\beta-1}\right)^i\frac{1}{j^2}-\ln(1-\beta)\sum_{i=1}^{n}\frac{1}{j}$$

$$\left.\times\left(\frac{\beta-1}{\beta}\right)^i+\sum_{i=2}^{n}\sum_{j=1}^{i-1}\frac{1}{ij}\left(\frac{\beta-1}{\beta}\right)^{i-j}\right], \quad (A4)$$

$$H(0,n)=n!\left(\frac{\pi^2}{6}-\sum_{i=1}^{n}\frac{1}{i^2}\right),$$

$$A(\beta,n)=\left(\frac{1}{1-\beta}\right)^n.$$

To tabulate these functions for the required values of β we sum the following infinite series.

$$\sum_{j=1}^{\infty}\frac{(-1)^j}{j^2}\left(\frac{0.45}{0.55}\right)^j = -0.69310353,$$

$$\sum_{j=1}^{\infty}\frac{1}{j^2}\left(\frac{0.55}{1.55}\right)^j = 0.39257179.$$

Rather than the functions (A1, A2, A3, A4) defined above we actually need certain linear combinations of these functions. For any $C(\beta,n)$ we define:

$$C_{ss}(\beta(\sigma),n)\equiv C[\beta(\sigma),n]+C[\beta(-\sigma),n]$$
$$-2C[\beta(0),n],$$

$$C_{sc}(\beta(\sigma),n)\equiv C[\beta(\sigma),n]-C[\beta(-\sigma),n], \quad (A5)$$

$$C_{cc}(\beta(\sigma),n)\equiv C[\beta(\sigma),n]+C[\beta(-\sigma),n]$$
$$+2C[\beta(0),n].$$

The symbols $C_{ss,\,sc,\,cc}(\beta,n)$ which occur in the following formulas should be interpreted as follows. For $\sinh^2\tfrac{1}{2}\sigma t$ integrals use $C_{ss}(\beta,n)$, for $\sinh\tfrac{1}{2}\sigma t\,\cosh\tfrac{1}{2}\sigma t$ integrals use $C_{sc}(\beta,n)$, for $\cosh^2\tfrac{1}{2}\sigma t$ integrals use $C_{cc}(\beta,n)$.

For $p \geqslant 0$, $q \geqslant 0$, $r \geqslant 0$,

$$U(p,q,r,d)\equiv\int_0^{\infty}ds\int_0^{s}du\int_0^{u}dt\,e^{-s}s^p t^q u^r\begin{Bmatrix}\sinh^2\tfrac{1}{2}\sigma t\\ \sinh\tfrac{1}{2}\sigma t\,\cosh\tfrac{1}{2}\sigma t\\ \cosh^2\tfrac{1}{2}\sigma t\end{Bmatrix}=\tfrac{1}{4}\frac{1}{r+1}$$

$$\times\left[(p+r+1)!\sum_{j=0}^{p+r+1}\frac{(q+j)!}{j!}A_{ss,\,sc,\,cc}(\sigma,q+j+1)-p!\sum_{j=0}^{p}\frac{(q+r+1+j)!}{j!}A_{ss,\,sc,\,cc}(\sigma,q+r+2+j)\right]. \quad (A6)$$

For $p \geqslant 0$, $q \geqslant 0$,

$$U(p,q,-1,d)\equiv\int_0^{\infty}ds\int_0^{s}du\int_0^{u}dt\,e^{-s}\frac{s^p t^q}{u}\begin{Bmatrix}\sinh^2\tfrac{1}{2}\sigma t\\ \sinh\tfrac{1}{2}\sigma t\,\cosh\tfrac{1}{2}\sigma t\\ \cosh^2\tfrac{1}{2}\sigma t\end{Bmatrix}$$

$$=\tfrac{1}{4}\left[p!\sum_{j=0}^{p-1}\sum_{k=0}^{j}\frac{(q+k)!}{k!(j+1)}A_{ss,\,sc,\,cc}(\sigma,q+k+1)+p!Y_{ss,\,sc,\,cc}(\sigma,q)\right]. \quad (A7)$$

For $p \geqslant 1$, $q \geqslant 1$,

$$U(p,q,-2,d)\equiv\int_0^{\infty}ds\int_0^{s}du\int_0^{u}dt\,e^{-s}\frac{s^p t^q}{u^2}\begin{Bmatrix}\sinh^2\tfrac{1}{2}\sigma t\\ \sinh\tfrac{1}{2}\sigma t\,\cosh\tfrac{1}{2}\sigma t\\ \cosh^2\tfrac{1}{2}\sigma t\end{Bmatrix}$$

$$=\tfrac{1}{4}\left[(p-1)!\sum_{j=0}^{p-1}\frac{(p-j)(q+j-1)!}{j!}A_{ss,\,sc,\,cc}(\sigma,q+j)\right]. \quad (A8)$$

For $q \geqslant 1$,

$$U(0,q,-2,d)\equiv\int_0^{\infty}ds\int_0^{s}du\int_0^{u}dt\,\frac{e^{-s}t^q}{u^2}\begin{Bmatrix}\sinh^2\tfrac{1}{2}\sigma t\\ \sinh\tfrac{1}{2}\sigma t\,\cosh\tfrac{1}{2}\sigma t\\ \cosh^2\tfrac{1}{2}\sigma t\end{Bmatrix}=\tfrac{1}{4}[(q-1)!A_{ss,\,sc,\,cc}(\sigma,q)-Y_{ss,\,sc,\,cc}(\sigma,q)]. \quad (A9)$$

For $p \geqslant 0$, $r \geqslant 0$,

$$V(p,q,r,d) \equiv \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s} \frac{s^p t^q u^r}{s+t} \left\{ \begin{array}{l} \sinh^2 \tfrac{1}{2}\sigma t \\ \sinh\tfrac{1}{2}\sigma t \cosh\tfrac{1}{2}\sigma t \\ \cosh^2\tfrac{1}{2}\sigma t \end{array} \right\}$$

$$= \tfrac{1}{4} \frac{1}{r+1} \left[\sum_{j=0}^{p+r} \sum_{k=0}^{j} \frac{(-1)^{p+r+j} j!(p+q+r+k-j)!}{k!} A_{ss,\,sc,\,cc}(\sigma, p+q+r+1+k-j) \right.$$

$$+ \sum_{j=0}^{p-1} \sum_{k=0}^{j} \frac{(-1)^{p+j} j!(p+q+r+k-j)!}{k!} A_{ss,\,sc,\,cc}(\sigma, p+q+r+1+k-j)$$

$$\left. + \frac{(-1)^p [(-1)^{r+1}-1]}{2^{p+q+r+2}} Y_{ss,\,sc,\,cc}[\tfrac{1}{2}(\sigma+1), p+q+r+1] \right]. \quad (A10)$$

For $p \geqslant 0$, $q \geqslant 0$,

$$V(p, q, -1, d) \equiv \int_0^\infty ds \int_0^s du \int_0^u dt \frac{e^{-s} s^p t^q}{u(s+t)} \left\{ \begin{array}{l} \sinh^2 \tfrac{1}{2}\sigma t \\ \sinh\tfrac{1}{2}\sigma t \cosh\tfrac{1}{2}\sigma t \\ \cosh^2\tfrac{1}{2}\sigma t \end{array} \right\}$$

$$= \tfrac{1}{4} \left[\sum_{j=0}^{p-1} \sum_{k=0}^{j-1} \sum_{l=0}^{k} \frac{(-1)^{p+1+j} j!(p+q+l-j-1)!}{(k+1)l!} A_{ss,\,sc,\,cc}(\sigma, p+q+l-j) \right.$$

$$\left. + \sum_{j=0}^{p-1} (-1)^{p+1+j} j! Y_{ss,\,sc,\,cc}(\sigma, p+q-j-1) + \frac{(-1)^p}{2} L_{ss,\,sc,\,cc}(1+\sigma, p+q) \right]. \quad (A11)$$

For $p \geqslant 0$, $q \geqslant 0$, $r \geqslant 0$,

$$W(p,q,r,d) \equiv \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-s} \frac{s^p t^q u^r}{s-t} \left\{ \begin{array}{l} \sinh^2 \tfrac{1}{2}\sigma t \\ \sinh\tfrac{1}{2}\sigma t \cosh\tfrac{1}{2}\sigma t \\ \cosh^2\tfrac{1}{2}\sigma t \end{array} \right\}$$

$$= \tfrac{1}{4} \frac{1}{r+1} \left[\sum_{j=0}^{p+r} \sum_{k=0}^{j} \frac{j!(p+q+r+k-j)!}{k!} A_{ss,\,sc,\,cc}(\sigma, p+q+r+1+k-j) \right.$$

$$\left. - \sum_{j=0}^{p-1} \sum_{k=0}^{j} \frac{j!(p+q+r+k-j)!}{k!} A_{ss,\,sc,\,cc}(\sigma, p+q+r+1+k-j) \right]. \quad (A12)$$

For $p \geqslant 0$, $q \geqslant 0$,

$$W(p, q, -1, d) \equiv \int_0^\infty ds \int_0^s du \int_0^u dt \frac{e^{-s} s^p t^q}{u(s-t)} \left\{ \begin{array}{l} \sinh^2 \tfrac{1}{2}\sigma t \\ \sinh\tfrac{1}{2}\sigma t \cosh\tfrac{1}{2}\sigma t \\ \cosh^2\tfrac{1}{2}\sigma t \end{array} \right\}$$

$$= \tfrac{1}{4} \left[\sum_{j=0}^{p-1} \sum_{k=0}^{j-1} \sum_{l=0}^{k} \frac{j!(p+q+l-j-1)!}{l!(k+1)} A_{ss,\,sc,\,cc}(\sigma, p+q+l-j) \right.$$

$$\left. + \sum_{j=0}^{p-1} j! Y_{ss,\,sc,\,cc}(\sigma, p+q-j-1) + H_{ss,\,sc,\,cc}(\sigma, p+q) \right]. \quad (A13)$$

APPENDIX B

All computations were done on an IBM. 650 computer, a medium-size machine with 2000 storage locations. First all functions such as $Y_{ss}(\beta,n)$ were tabulated and used in computation of the integrals. There were some 600 integrals of each type. Next the matrices associated with each operator were found, and finally we computed the expectation values of these operators.

For a computation of this size many checks are necessary. A typical example is the following. The fastest way to generate the $Y(\beta,n)$ is by the recursion formula. In addition, however, we employed the explicit formula

for $Y(\beta,n)$ to find its value for a large n and compared it with the value predicted by recursion.

Almost all matrices encountered were symmetric. This property was used as a check in the initial phases of each machine computation.

The most powerful check was the following. We chose $f_i(\tfrac{1}{2}\sigma t) = \cosh(\tfrac{1}{2}\sigma t)$, took $\sigma = 0$, and picked p_i, q_i, r_i so that we had functions suitable for the ground state. By setting $\sigma = 0$ in our programs we tabulated functions, integrals, and matrices for this state. All energy corrections were then calculated and compared with published results.