

# Calculations in Schrödinger Perturbation Theory\*

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The evaluation of second- and higher-order perturbations of the energy by iterative solution of Schrödinger's equation, rather than by evaluation of the well-known matrix formulas, is described and exploited. Several examples are worked out exactly for the hydrogen atom, to point the way for other more practical, but more involved, problems.

## I. INTRODUCTION

Schrödinger perturbation theory deals with the attempted solution of the eigenvalue problem

$$H\psi = E\psi,$$

where  $H = H_0 + H'$  contains a zeroth order part  $H_0$  and the perturbation  $H'$ . Expanding strictly in powers of the "smallness" of  $H'$ , we have the well-known matrix solution

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots,$$

$$\psi = \psi^{(0)} + \psi^{(1)} + \dots,$$

$$E_m^{(0)} |m\rangle = H_0 |m\rangle, \quad E_m^{(1)} = \langle m | H' | m \rangle,$$

$$E_m^{(2)} = \sum_n' \frac{\langle m | H' | n \rangle \langle n | H' | m \rangle}{E_m^{(0)} - E_n^{(0)}}, \quad (1)$$

$$\psi_m^{(1)} = \sum_n' |n\rangle \frac{\langle n | H' | m \rangle}{E_m^{(0)} - E_n^{(0)}}, \quad (2)$$

where  $|n\rangle$  are the complete set of eigenstates ( $\psi_n^{(0)}$ ) of  $H_0$ . The practical problem at hand is that while the expression for  $E^{(1)}$  is simple enough (just a single integral need be done), that for  $E^{(2)}$  is so complicated (an infinite sum over integrals) that one seldom can evaluate beyond first-order energy shift without making some gross approximations.

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As an alternative to the above popular matrix solution, one can simply write down the complete Schrödinger equation, order by order

$$\begin{aligned} (E_m^{(0)} - H_0)\psi_m^{(0)} &= 0, \\ (E_m^{(0)} - H_0)\psi_m^{(1)} &= (H' - E_m^{(1)})\psi_m^{(0)}, \end{aligned} \quad (1')$$

$$E_m^{(1)} = \int \psi_m^{(0)*} H' \psi_m^{(0)} d\tau,$$

$$E_m^{(2)} = \int \psi_m^{(0)*} (H' - E_m^{(1)})\psi_m^{(1)} d\tau, \quad (2')$$

and try to solve the differential Eq. (1') for  $\psi^{(1)}$ .

The complete equivalence of the two formulations of the problem is quite easily seen, and it has been mentioned (1) that it might be easier in some cases to work from (1'), (2') instead of (1). However, it seems that only recently (2) has this possibility been realized in practice.

There are two dynamical systems which can be completely solved and might serve as  $H_0$ 's for many problems: the harmonic oscillator, and the hydrogen atom. For perturbations on the harmonic oscillator the matrix formulation (1) is most powerful, since the simple operators  $x^n$ ,  $p^n$  have only a few, easily calculable, nonzero matrix elements. The recent work by Dalgarno (2) and collaborators has shown that the differential equation approach (1'), (2') is the most effective way to evaluate many perturbations on the hydrogen atom system. It is this latter situation that we shall explore in this paper.

In Paper II of this series, we shall describe a very important application of these techniques in problems where we do not start with exact solutions of some  $H_0$ , but rather the approximate (trial) solutions of a given, complicated  $H$ . Finally in Paper III we give even more general mathematical techniques applicable only to the hydrogen atom model, and we carry out the difficult calculation of the nonrelativistic part of the Lamb shift.

## II. EXPOSITION: THE METHOD OF DALGARNO AND LEWIS

For general perturbation problems, we shall start with the matrix solution (1) for  $E^{(2)}$  and simplify notations by calling the state  $|m\rangle$ ,  $|0\rangle$ , and dropping superscript<sup>(0)</sup> on the energies in the denominator.

$$E^{(2)} = \sum_n' \frac{\langle 0 | H' | n \rangle \langle n | H' | 0 \rangle}{E_0 - E_n}, \quad (3)$$

also

$$\psi^{(1)} = \sum_n' |n\rangle \frac{\langle n | H' | 0 \rangle}{E_0 - E_n}. \quad (4)$$

Formula (3) is "evaluated" by defining an (Hermitian) operator  $F$  such that

$$[F, H_0] |0\rangle = (H' - E^{(1)}) |0\rangle, \quad (5)$$

whence

$$\begin{aligned} E^{(2)} &= \sum_n' \frac{\langle 0 | H' | n \rangle \langle n | FH_0 - H_0 F | 0 \rangle}{E_0 - E_n} \\ &= \sum_n' \langle 0 | H' | n \rangle \langle n | F | 0 \rangle \\ &= \langle 0 | H' F | 0 \rangle - E^{(1)} \langle 0 | F | 0 \rangle. \end{aligned} \quad (6)$$

This is the result for second-order perturbation to the energy in terms of a single integral only. The problem is to find  $F$ , which is given as the solution of Eq. (5)<sup>1</sup> for the particular state  $|0\rangle$  in question. The connection with Eqs. (1'), (2'), comes from substituting (5) into (4) whence

$$\psi^{(1)} = F |0\rangle - \langle 0 | F | 0 \rangle |0\rangle,$$

and Eq. (5) is

$$(E_0 - H_0)F |0\rangle = (H' - E^{(1)}) |0\rangle,$$

which is just Eq. (1'); similarly (6) is the same as (2').

The method is then useful only if we can find  $F$  satisfying (5). There are three approaches here that should be pointed out.

A. Assume  $F$  is a function of space coordinates only so that

$$[F, H_0] = \frac{\hbar^2}{2m} (\nabla^2 F + 2\nabla F \cdot \nabla).$$

We assume

$$\left[ H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}). \right]$$

Then by some good fortune manage to solve the inhomogeneous differential equation

$$\psi_0 \nabla^2 F + 2(\nabla F) \cdot (\nabla \psi_0) = \frac{2m}{\hbar^2} (H' - E^{(1)}) \psi_0. \quad (7)$$

The boundary conditions are clear when we remember that the wave function is  $\psi \approx (1 + F)\psi_0$ . In the next section of this paper, we shall display examples of this type of solution.

<sup>1</sup> One might try to solve the operator equation  $[F, H_0] = H' - E^{(1)}$  which would allow evaluation of  $E^{(2)}$  for every state, but this is in general much too hard. Instead we solve the much more special Eq. (5) for each state  $|0\rangle$ .

B. For any one-dimensional problem, (7) can be solved by quadrature (3)

$$F(x) = \frac{2m}{\hbar^2} \int^x \frac{dx'}{\psi_0^2(x')} \int^{x'} dx'' \psi_0(x'') (H' - E^{(1)}) \psi_0(x''), \quad (8)$$

where the unspecified lower limits of integration are determined by the boundary conditions.<sup>2</sup> We solve one problem by this method in the last section of this paper.

C. One may construct a variational principle for  $F$  as follows. Consider the quantity

$$J \equiv \langle 0 | \phi(H' - E^{(1)}) + (H' - E^{(1)})\phi - \frac{1}{2}[\phi, [\phi, H_0]] | 0 \rangle. \quad (9)$$

Straightforward calculation shows that  $J$  will be stationary with respect to arbitrary variations of the operator  $\phi$  if  $\phi$  satisfies Eq. (5) for  $F$  and its adjoint

$$\langle 0 | [H_0, F] = \langle 0 | (H' - E^{(1)}).$$

Furthermore if  $\phi$  does satisfy (5) then  $J = E^{(2)}$ , and we have a useful variational expression for  $E^{(2)}$  depending on our choice of  $\phi$  to approximate  $F$ . We can put (9) in homogeneous form by setting  $\phi = c\varphi$  and varying the constant  $c$ . We then have

$$\begin{aligned} c &= I_1/I_2, & J &= \frac{1}{2}I_1^2/I_2, \\ I_1 &= \langle 0 | \varphi(H' - E^{(1)}) + (H' - E^{(1)})\varphi | 0 \rangle, \\ I_2 &= \langle 0 | [\varphi, [\varphi, H_0]] | 0 \rangle. \end{aligned} \quad (10)$$

The connection with the Ritz variational principle for the total energy is easily established (see Refs. 3 and 1). An example of this variational calculation will be given in Paper number III of this series.

### III. EXAMPLES: SIMPLE SECOND-ORDER PERTURBATION CALCULATIONS IN HYDROGEN

The zeroth-order Hamiltonian is

$$H_0 = \frac{-\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \quad (11)$$

and for the ground (1s) state

$$\psi_0 \equiv |0\rangle = \sqrt{\frac{4/a^3}{4\pi}} e^{-r/a}, \quad (12)$$

where  $a = \hbar^2/Zme^2$ .

<sup>2</sup> It is seen that an arbitrary constant can always be added to  $F$  within the definition of Eq. (5); but this constant drops out in calculation of  $E^{(2)}$ , Eq. (6).

Consider the perturbation by a  $2^l$  multipolar electrostatic potential with infinitely removed sources.

$$H' = -e\lambda P_l(\cos \theta)r^l \quad (l > 0), \quad (13)$$

where  $P_l$  is the  $l$ th Legendre polynomial and  $\lambda$  gives the strength of the field. For the ground state  $E^{(1)}$  vanishes so we calculate  $E^{(2)}$  for the polarization energy. To calculate all the Coulomb matrix elements of (13) would be hard work, and to sum the series (1) appears impossible. Solution of Eq. (5) for  $F$  is, however, quite simple. Dividing Eq. (7) by  $\psi_0$ , we have

$$\nabla^2 F - \frac{2}{a} \frac{\partial}{\partial r} F = -\frac{2me\lambda}{\hbar^2} P_l(\cos \theta)r^l,$$

which is easily solved by variation of constants

$$F = \lambda P_l(\cos \theta)(\alpha r^l + \beta r^{l+1}),$$

yielding

$$F = \frac{me\lambda}{\hbar^2} P_l(\cos \theta) \left( \frac{a^2 r^l}{l} + \frac{a r^{l+1}}{l+1} \right). \quad (14)$$

A simple integration then gives

$$E^{(2)} = -\lambda^2 \frac{(2l+1)!(l+2)}{l2^{2l+1}} \frac{a^{2l+1}}{Z}.$$

For  $l = 1$  we have the (dipole) polarizability

$$\alpha \equiv -\frac{2}{\lambda^2} E^{(2)} = \frac{9}{2} \frac{a^3}{Z},$$

a well-known result.

The long-range force between a hydrogen atom and a fixed charge some large distance  $R$  away was first calculated by Dalgarno and Lewis (2) exactly as we have just done. Later calculation (4) has given the exact second-order interaction for all distances  $R$  large and small.

Suppose that with the external multipole potential  $\lambda P_l r^l$  one attempts to measure the  $2^l$ -pole moment of the hydrogen nucleus. The electron will produce a shielding effect which reduces the effective field strength seen by the nucleus to

$$\lambda P_l r^l (1 - \gamma_l).$$

We can calculate  $\gamma_l$  by the mixed second-order perturbation calculation where the two interactions seen by the electron are  $H'$  (same as (13)) due to the external

field, and  $H'' = -e/r^{l+1}P_l(\cos \theta)$  due to interaction with the nuclear moment (given unit magnitude). We want

$$\gamma_l = -\frac{1}{\lambda} \sum'_n \frac{\langle 0 | H' | n \rangle \langle n | H'' | 0 \rangle + \langle 0 | H'' | n \rangle \langle n | H' | 0 \rangle}{E_0 - E_n},$$

which we evaluate to be

$$-\frac{2}{\lambda} \langle 0 | H'' F | 0 \rangle,$$

with  $F$  given by (14). The result of integration gives

$$\gamma_l = \frac{2}{Zl(l+1)}.$$

In the neutral atom ( $Z = 1$ ) the electric dipole field is thus completely screened, and the electric quadrapole field is reduced by  $\frac{1}{3}$  of its original value.

One could also have solved this problem by getting the  $F$  corresponding to  $H''$  on the right-hand side of (7). The solution for this  $F$  does not follow from (14) by the substitution  $l \rightarrow -l - 1$  since

$$\nabla^2 r^{-l-1} P_l(\cos \theta) = -P_l(\cos \theta)(l+1)r^{-l} \frac{\delta(r)}{r^2},$$

where  $\int_0^\infty dr f(r) \delta(r) = f(0)$ . The correct  $F$  solution generated by  $r^{-l-1} P_l(\cos \theta)$

has the form

$$P_l(\cos \theta) \sum_{m=-l+1}^0 c_m r^m.$$

The operator  $H' = \frac{2}{3} \mu_0 g_I \delta \cdot \mathbf{I} [\delta(r)/r^2]$  gives the hyperfine structure of  $s$ -electrons. The first order shift is (for the ground state)

$$E^{(1)} = \frac{2}{3} \mu_0 g_I \langle \delta \cdot \mathbf{I} \rangle \frac{4}{a^3},$$

which gives the first-order energy-level splitting

$$\Delta\nu^{(1)} = \frac{8}{3} \frac{\mu_0 g_I}{a^3} (2I + 1).$$

We want to calculate the interaction to second order for the electron, in order to get the next contribution to the energy-level splitting

$$\Delta\nu^{(2)} = -\left(\frac{2}{3} \mu_0 g_I\right)^2 (2I + 1) \sum'_n \frac{\langle 0 | \frac{\delta(r)}{r^2} | n \rangle^2}{E_0 - E_n}.$$

The equation for  $F$  is

$$\left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{a} \frac{d}{dr} \right] F = \frac{2m}{\hbar^2} \left( \frac{\delta(r)}{r^2} - \frac{4}{a^3} \right),$$

which has the solution

$$F = \frac{2m}{\hbar^2} \left( -\frac{1}{r} + \frac{2}{a} \ln r + \frac{2r}{a^2} \right). \quad (15)$$

It is easily seen that  $\Delta\nu^{(2)}$  is infinite due to the singular nature of  $H'$ ; actually the small distance behavior would be modified by relativistic and other (e.g., nuclear size) effects to yield a finite, and in fact small, result. However it will be of interest for us to compare this second-order calculation for two different states and get a result which is finite in our calculation, and would therefore not depend on the "cutoff" of a more refined theory. Heberle *et al.* (5) have measured the ratio of  $\Delta\nu$ 's in the 1s and 2s states of hydrogen to very high accuracy, and Mittleman (6) has given an account of the small residual effects in terms of quantum electrodynamical corrections. He did, however, not include such an effect as this second-order hfs.

For the 2s state we find

$$\Delta\nu_{2s}^{(1)} = \frac{1}{8} \Delta\nu_{1s}^{(1)},$$

$$F_{2s} = \frac{2m}{\hbar^2} \left( -\frac{1}{r} + \frac{2}{a} \ln r + \frac{r}{2a^2} + \frac{7}{(2a-r)} \right).$$

Of interest is the residual  $R$  defined by

$$\frac{\Delta\nu_{2s}}{\Delta\nu_{1s}} = \frac{1}{8} (1 + R),$$

whence

$$R = \frac{8\Delta\nu_{2s}^{(2)} - \Delta\nu_{1s}^{(2)}}{\Delta\nu_{1s}^{(1)}} = -\frac{a^3}{4} \frac{2}{3} \mu_0 g_I$$

$$\cdot \left\{ 8 \langle 2s \left| \frac{\delta(r)}{r^2} F_{2s} \right| 2s \rangle - 8 \langle 2s \left| \frac{\delta(r)}{r^2} \right| 2s \rangle \langle 2s | F_{2s} | 2s \rangle \right.$$

$$\left. - \langle 1s \left| \frac{\delta(r)}{r^2} F_{1s} \right| 1s \rangle + \langle 1s \left| \frac{\delta(r)}{r^2} \right| 1s \rangle \langle 1s | F_{1s} | 1s \rangle \right\},$$

which works out to yield<sup>3</sup>

$$R = -\frac{4m\mu_0 g_I}{3\hbar^2 a} (3 - 2 \ln 2) = -\alpha^2 \frac{m}{M} g_I \left(1 - \frac{2}{3} \ln 2\right)$$

in terms of the fine-structure constant  $\alpha$ , electron to proton mass ratio  $m/M$ , and the nuclear  $g$ -factor  $g_I$  (= nuclear moment in units of  $e\hbar/2Mc$  divided by nuclear spin).

This is not yet the entire effect since the hyperfine structure interaction can also couple  $s_{1/2}$  states to  $d_{3/2}$  state through the interaction

$$H'' = 2\mu_0 g_I \left( \nabla \frac{\mathbf{I} \cdot \mathbf{r}}{r^3} \right) \cdot (1 - \mathbf{s}).$$

The calculation of this in second-order proceeds as before.

$$\Delta v_{s-d}^{(2)} = 5\mu_0^2 g_I^2 (2I + 1) \sum_n' \frac{\langle 0 | r^{-3} P_2(\cos \theta) | n \rangle^2}{E_0 - E_n}.$$

The appropriate  $F$ 's are

$$\begin{aligned} F_{1s} &= -\frac{2m}{\hbar^2} \frac{1}{6} P_2(\cos \theta) \left( \frac{1}{r} + \frac{1}{3a} \right), \\ F_{2s} &= \frac{-2m}{\hbar^2} \frac{1}{6} P_2(\cos \theta) \left( \frac{1}{r} + \frac{1}{12a} + \frac{1}{(4a - 2r)} \right), \end{aligned} \tag{16}$$

and we have the result

$$R_{s-d} = -\alpha^2 \frac{m}{M} g_I \frac{1}{8} \left( \frac{17}{16} - \frac{5}{3} \ln 2 \right).$$

The  $s$ - $d$  contribution is very much smaller than the  $s$ - $s$  part, and the combined result is

$$R_{s-s} + R_{s-d} = -0.153 \times 10^{-7} g_I.$$

In hydrogen ( $g_I = 5.58$ ) this contributes  $-0.85 \times 10^{-7}$  to the experimental value of  $(13 \pm 3) \times 10^{-7}$ . This effect alone does not resolve the discrepancy between this measured value and the result of Mittleman's calculation ( $20.5 \times$

<sup>3</sup> M. H. Mittleman (private communication) has calculated this effect working from the Dirac equation and making the appropriate  $\alpha^2$  approximations. His result

$$R = -\alpha^2 \frac{m}{M} g_I \left( \frac{17}{12} - \frac{4}{3} \ln 2 \right)$$

is different from ours (although only 12 percent larger in numerical value). We have been unable to understand this difference.



$10^{-7}$ ), but suggests that there may be other important  $\alpha^2 m/M$  corrections (from relativistic recoil of proton, etc.)

#### IV. EXAMPLE: A THIRD-ORDER PERTURBATION CALCULATION

We shall now calculate the Stark effect on the hyperfine structure of hydrogen in the ground state. The total perturbation is

$$H' = -e\mathcal{E}r \cos \theta + \text{hfs}$$

where hfs = the two parts of the hyperfine structure interaction given in the preceding section. In first order this  $H'$  gives only the first order splitting of the hfs levels. In second order, we get the quadratic Stark effect, which is the same shift for both hfs levels, and also the second-order hfs just discussed. Finally, in third order, we find a new, interesting effect: the change in the hfs splitting which depends on the external electric field strength ( $\sim \mathcal{E}^2$ ). The relevant part of the third-order energy formula is

$$\begin{aligned} E^{(3)} = & 2 \sum'_m \sum'_n \frac{\langle 0 | e\mathcal{E}r \cos \theta | n \rangle \langle n | e\mathcal{E}r \cos \theta | m \rangle \langle m | \text{hfs} | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} \\ & + \sum'_m \sum'_n \frac{\langle 0 | e\mathcal{E}r \cos \theta | n \rangle \langle n | \text{hfs} | m \rangle \langle m | e\mathcal{E}r \cos \theta | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} \\ & - \langle 0 | \text{hfs} | 0 \rangle \sum'_m \frac{\langle 0 | e\mathcal{E}r \cos \theta | m \rangle^2}{(E_0 - E_m)^2}. \end{aligned} \quad (17)$$

To evaluate  $E^{(3)}$  we first find an operator  $F$  such that

$$[F, H_0] | 0 \rangle = e\mathcal{E}r \cos \theta | 0 \rangle, \quad (18)$$

which lets us reduce (17)

$$\begin{aligned} E^{(3)} = & 2 \sum'_m \frac{\langle 0 | F e\mathcal{E}r \cos \theta | m \rangle \langle m | \text{hfs} | 0 \rangle}{E_0 - E_m} \\ & + \langle | F \text{hfs} F | 0 \rangle - \langle 0 | \text{hfs} | 0 \rangle \langle 0 | F^2 | 0 \rangle. \end{aligned}$$

We already know the solution of (18):

$$F = \frac{2m}{\hbar^2} e\mathcal{E} \cos \theta \left( -\frac{a^2 r}{2} - \frac{ar^2}{4} \right).$$

To reduce the one remaining sum we seek another operator  $G$  defined by

$$[G, H_0] | 0 \rangle = F e\mathcal{E}r \cos \theta | 0 \rangle - \langle 0 | F e\mathcal{E}r \cos \theta | 0 \rangle | 0 \rangle$$

to get

$$E^{(3)} = \langle 0 | (F^2 + 2G)\text{hfs} | 0 \rangle - \langle 0 | F^2 + 2G | 0 \rangle \langle 0 | \text{hfs} | 0 \rangle.$$

We find

$$G = \left( \frac{2me\varepsilon}{\hbar^2} \right)^2 \left\{ \frac{a^2 r^4}{96} + \frac{a^3 r^3}{16} + \frac{3a^4 r^2}{16} + \frac{2}{3} P_2(\cos \theta) \left( \frac{a^2 r^4}{32} + \frac{5a^3 r^3}{32} + \frac{15a^4 r^2}{64} \right) \right\}.$$

Evaluating the remaining integrals in  $E^{(3)}$  we get a shift  $\delta(\varepsilon)$  in the separation of the two hfs levels given by

$$\delta(\varepsilon) = - \frac{1193}{80} \Delta\nu e^2 \varepsilon^2 a^6 \frac{m^2}{\hbar^4}$$

and thus for hydrogen ( $a = \hbar^2/m\varepsilon^2$ ) a fractional shift in the resonance frequency.

$$\frac{\delta(\varepsilon)}{\Delta\nu} = - 14.91 \frac{\varepsilon^2 a_0^3}{(e^2/a_0)},$$

which has the expected form: second order Stark shift  $\div$  Rydberg.

In discussing the presumed "pressure shift" occurring in their measurement of  $\Delta\nu$ , Wittke and Dicke (7) estimated this effect simply by using the characteristic dimensions of the system. We now see that they underestimate the result by a factor of fifteen. The result of this calculation gives also a qualitative understanding of the result of the experiment by Haun and Zacharias (8) on the Stark effect on the hfs in cesium.

#### V. ATTEMPTS TO STUDY THE HELIUM ATOM

The separation of the 2-electron atom Hamiltonian into

$$H_0 = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - Ze^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \tag{19}$$

and

$$H' = \frac{e^2}{r_{12}}$$

gives, in treating  $H'$  as a perturbation, a power series in  $1/Z$  for the energy. For the ground state

$$E = \left\{ -2Z^2 + \frac{5}{4}Z - E_2 + 0 \left( \frac{1}{Z} \right) \dots \right\} \frac{e^2}{2a_0}. \tag{20}$$

The calculation of  $E_2$  has been the subject of much work by Hylleraas (see Ref. 1, Section 33) using the variational principle. We have tried, but not succeeded, to calculate  $E_2$  by analytical means. Even though the expansion (20) is not very

useful as a means of calculating the energy of the He atom, an exact evaluation of  $E_2$  would provide a standard to which one could compare Hylleraas' result in order to judge how appropriate is his choice of trial functions. In this direction of supplying some exact answers with which to gauge the accuracy of trial functions, we find that we can evaluate the first correction to the one-electron density.

The zeroth-order wave function is

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi} \frac{4}{a^3} e^{-(r_1+r_2)/a}$$

and the first-order correction to this due to the above  $H'$  is

$$\psi^{(1)} = \sum'_n |n\rangle \frac{\langle n | \frac{e^2}{r_{12}} | 0 \rangle}{E_0 - E_n},$$

where  $|n\rangle$  are all the hydrogenic states for two electrons (space-symmetric for the spin singlet under consideration). The square of the total wave function  $\psi_0 + \psi^{(1)} + \dots$  integrated over the coordinates of electron No. 2 gives the one-body density  $\rho(\mathbf{r}_1)$ . To first order we have

$$\begin{aligned} \rho(\mathbf{r}_1) &= \int |\psi_0(\mathbf{r}_1, \mathbf{r}_2)|^2 dv_2 + 2 \int \psi_0(\mathbf{r}_1, \mathbf{r}_2) \psi^{(1)}(\mathbf{r}_1, \mathbf{r}_2) dv_2 \\ &\equiv \frac{1}{4\pi} \frac{4}{a^3} e^{-2r_1/a} \left[ 1 + \frac{2}{Z} \chi(r_1) \right], \end{aligned} \quad (21)$$

where  $\chi(r)$  includes the first-order effects of the correlation  $e^2/r_{12}$ . The states  $|n\rangle$  in  $\psi^{(1)}$  can be written

$$\begin{aligned} |n\rangle &= \sum_m [u_{n_1 l m}(\mathbf{r}_1) u_{n_2 l-m}(\mathbf{r}_2) + u_{n_1 l m}(\mathbf{r}_2) u_{n_2 l-m}(\mathbf{r}_1)] \\ &\quad \cdot (2(1 + \delta_{n_1 n_2}))^{-1/2} \frac{(-1)^{l-m}}{\sqrt{2l+1}}, \end{aligned}$$

where  $u_{nlm}$  are hydrogen states and the two orbitals are coupled to a total  $S$ -state. In calculating  $\chi$  we keep only those states in which one electron stays in the  $1s$  orbit. This is no approximation, but is forced by the integration over  $\mathbf{r}_2$  in Eq. (21). Thus, we are reduced to the one-electron problem

$$\frac{1}{Z} \chi(r) |0\rangle = 2 \sum'_n |n\rangle \frac{\langle n | V | 0 \rangle}{E_0 - E_n},$$

where

$$V(r) = \langle 1s | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | 1s \rangle = \frac{e^2}{r} \left[ 1 - e^{-2r/a} \left( 1 + \frac{r}{a} \right) \right]$$

and

$$\langle 0 | V | 0 \rangle = E^{(1)} = \frac{5}{4} Z \frac{e^2}{2a_0}. \tag{22}$$

From our earlier studies we see that

$$\frac{1}{Z} \chi = 2[F - \langle 0 | F | 0 \rangle],$$

where

$$[F, H_0] | 0 \rangle = [V - \langle 0 | V | 0 \rangle] | 0 \rangle.$$

This is just the type of one dimensional problem referred to in paragraph B of Section II, and we solve by integration.

$$F = \frac{2m}{\hbar^2} \int_0^r \frac{dr}{r^2 \psi_0^2} \int_0^r dr r^2 \psi_0^2 [V - \langle 0 | V | 0 \rangle] = \frac{2}{Z} \left\{ \frac{3}{8} \int_0^r dr \left( \frac{e^{-2r/a} - 1}{r} \right) - \frac{3}{16} a \left( \frac{e^{-2r/a} - 1}{r} \right) + \frac{5}{8} \frac{r}{a} - \frac{1}{4} e^{-2r/a} - \frac{1}{8} \right\} \tag{23}$$

and

$$\langle 0 | F | 0 \rangle = \frac{2}{Z} \left( \frac{19}{32} - \frac{3}{8} \ln 2 \right). \tag{24}$$

In the variable  $x = 2r/a$  we have finally

$$\frac{1}{2} \chi(x) = -\frac{23}{32} - \frac{3}{8} C - \frac{3}{8} \ln \frac{x}{2} - \frac{1}{4} e^{-x} + \frac{5}{16} x - \frac{3}{8} \frac{e^{-x} - 1}{x} + \frac{3}{8} Ei(-x) \tag{25}$$

$$C = +.5772 \dots, \quad Ei(-x) = - \int_x^\infty \frac{e^{-s}}{s} ds.$$

Hylleraas [see Bethe (1), p. 238] gives the wave function as

$$U_0 \left[ 1 + \frac{1}{Z} \varphi \right], \quad U_0 = e^{-1/2\sigma} \frac{1}{4\pi} \frac{4}{a^3}, \quad \varphi = \sum c_{nlm} \sigma^n r^{2l} v^m, \tag{26}$$

where

$$\sigma = 2 \frac{r_1 + r_2}{a}, \quad \tau = 2 \frac{r_1 - r_2}{a}, \quad v = 2 \frac{r_{12}}{a}.$$

Thus

$$\chi_H(\mathbf{r}_1) = \frac{1}{\pi a^3} \int dv_2 \varphi(\mathbf{r}_1, \mathbf{r}_2) e^{-2r_2/a}. \tag{27}$$

TABLE I  
COMPARISON OF THE EXACT RESULT WITH HYLLERAAAS' 8-PARAMETER APPROXIMATE  
1/Z-CORRECTION TO THE ONE-ELECTRON DENSITY IN HELIUM

$x$	0	0.5	1	2	4	
$\chi$	-0.33382	-0.32554	-0.29999	-0.20026	+0.14089	+1.09170
$\chi_H$	-0.33	-0.328	-0.300	-0.199	+0.138	+1.102

The various integrals in (27) are easily evaluated. We give here the result for Hylleraas' 8-parameter function  $(1)^4 x = 2r/a$ ,

$$\chi_H(x) = -0.889 + 0.1719x + 0.0109x^2 - 0.0035x^3 \\ - 0.2343e^{-x} - 0.00944xe^{-x} + 0.785 \frac{1 - e^{-x}}{x}.$$

A numerical comparison between  $\chi_H$  and our exact  $\chi$  is given in Table I. The errors in the one-body density from Hylleraas' 8-parameter function are thus seen to be about 1 percent, while the energy  $E_2$  obtained with that wave function is within 0.2 percent of the value from a much more complicated function (9).<sup>5</sup> We cannot use our exact  $\chi$  to calculate  $E_2$  since that requires knowledge of the two-body density. It will be interesting to repeat this comparison with Hylleraas' more recent work (9) (up to 24 parameters) to see just how effective the newly added terms are. The error shown here may be a useful guide in deciding how to improve the trial function at each step.

## VI. SUMMARY

We have explored the technique of evaluating second-order perturbation theory, from the point of view of Schrödinger's differential equation. The method seems very well adaptable to problems based on the hydrogen atom and several examples—some of these actually of practical interest—have been worked out. In the following two papers we present further generalized applications of this technique.

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<sup>4</sup> A constant has been added to  $\varphi$  in order to make  $U_{\varphi\varphi}$  orthogonal to  $U_0$  as required by the perturbation theory.

<sup>5</sup> The errors in the actual 2-body wave function are probably of the order of 5 percent, but the calculation of  $\rho(r_1)$  already smooths out some of this error.

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