# Uses of Approximate Wave Functions*

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A procedure is given for using approximate wave functions (derived, say, by the Ritz variational method), to calculate properties of the system other than the energy to an accuracy much greater than that previously thought to be possible. The method is based on the form of perturbation theory discussed in the previous paper but stands by itself as an independent and, it is believed, very powerful innovation. Several sample problems, based on the two-electron atom, are worked out; and a program of greatly increasing the accuracy in the calculation of many properties of atomic systems is envisaged.

## I. INTRODUCTION

It is well known that an approximate wave function $\psi_0$, when used in the Ritz variational principle

$$[E] = \frac{(\psi_0, H\psi_0)}{(\psi_0, \psi_0)} = \text{minimum}$$

gives an approximation $[E]$ to the true energy $E$ which is in error by terms of second order in the (small) difference between $\psi_0$ and the exact solution $\psi$ obeying

$$H\psi = E\psi.$$

If, however, one wants to calculate some other property of this state of the system, which would be given by the first-order perturbation theory as

$$(\psi, \Omega\psi),$$

where $\Omega$ is some operator which does not commute with $H$, then the evaluation of

$$(\psi_0, \Omega\psi_0)$$

gives an answer which is in error by terms of the first order in $\Delta \equiv \psi - \psi_0$.

One way of improving the calculation would be to imagine $\psi_0$ as the eigenfunction of some Hamiltonian $H_0$, and then treat the difference between $H$ and $H_0$ as a perturbation. The correction to $(\psi_0, \Omega\psi_0)$ would then appear as a second-order perturbation calculation mixing the two perturbations $\Omega$ and $H - H_0$.

From the viewpoint of the matrix formulation of second-order perturbation theory this would seem like an impossible calculation; but from the iterated differential equation approach described in the preceding paper ($1$) one could perhaps simply solve the equation

$$[F, H_0]\psi_0 = \Omega\psi_0 - (\psi_0, \Omega\psi_0)\psi_0$$

for $F$, and then calculate

$$2(\psi_0, F(H - H_0)\psi_0).$$

This is the type of solution we seek for the problem of calculating $(\psi, \Omega\psi)$ more accurately, although we shall not have to consider any zeroth-order Hamiltonian $H_0$, nor shall we explicitly do perturbation theory.

In what follows, we have $H\psi = E\psi$, $\psi = \psi_0 + \Delta$ where $\Delta$ is the (presumed small) error in the trial function $\psi_0$. Without loss of generality we may take $(\psi_0, \Delta) = 0$ and normalize both wave functions

$$(\psi, \psi) \approx (\psi_0, \psi_0) \approx 0,$$

where the symbol $\approx$ will mean "equal to within terms of order $\Delta^2$." The Ritz energy is

$$[E] = \frac{(\psi_0, H\psi_0)}{(\psi_0, \psi_0)} \approx (\psi, H\psi) - (\Delta, H\psi_0) - (\psi_0, H\Delta)$$

$$\approx (\psi, H\psi) - (\Delta, H\psi) - (\psi, H\Delta)$$

$$\approx E[1 - (\Delta, \psi_0) - (\psi_0, \Delta)] = E,$$

which thus errs by $0(\Delta^2)$ as stated.

For the approximation to $(\psi, \Omega\psi)/(\psi, \psi) \equiv \langle\Omega\rangle$, we shall define

$$[\Omega] \equiv \frac{(\psi_0 \mid \Omega + F(H - \epsilon) + (H - \epsilon)F \mid \psi_0)}{(\psi_0, \psi_0)} \tag{1}$$

and determine the (Hermitian) operator $F$ which makes $[\Omega] - \langle\Omega\rangle$ second order small in $\Delta$. In formula (1) $H$ is the full Hamiltonian and $\epsilon$ will be either $E$ or $[E]$, which are $\approx$ to each other.

Now, using $(H - \epsilon)\psi \approx 0$ we proceed to calculate

$$[\Omega] - \langle\Omega\rangle \approx (\psi, \Omega\psi) - (\Delta, \Omega\psi) - (\psi, \Omega\Delta)$$

$$- (\psi, F(H - \epsilon)\Delta) - (\Delta, (H - \epsilon)F\psi) - (\psi, \Omega\psi)$$

$$\approx -(\Delta, \Omega\psi_0) - (\psi_0, \Omega\Delta) - (\psi, [F, H]\Delta) - (\Delta, [H, F]\psi)$$

$$\approx (\Delta \mid [F, H] - \Omega \mid \psi_0) + (\psi_0 \mid [H, F] - \Omega \mid \Delta).$$

These are the first order (in $\Delta$) errors which we want to vanish. We thus require

$$[F, H]\psi_0 = \Omega\psi_0 - \frac{(\psi_0, \Omega\psi_0)}{(\psi_0, \psi_0)}\psi_0, \tag{2}$$

which is the equation determining $F$. Note that this looks just like the perturbation theory, but we never had to postulate $\psi_0$ as the eigenfunction of some $H_0$. The practical use of this method lies in the fact that (1) and (2) involve only the one function $\psi_0$.

The problem is now to solve (2) for $F$. There are three courses open.

$A$. Use a simple enough $\psi_0$ so that one can solve (2) by either analytical or numerical means. Remember that for a one-dimensional problem, one can always find $F$ by direct integration.

$B$. Use the stationary expression

$$J = (\psi_0 \mid \tfrac{1}{2}[F, [F, H]] - F(\Omega - \langle\Omega\rangle) - (\Omega - \langle\Omega\rangle)F \mid \psi_0)$$

to get the "best" value for some guessed solution $F$, such as $F = \Omega(c_1 + c_2r + \cdots)$, for example.

$C$. Suppose one has some accurate but complicated $\psi_0$ for which it seems too difficult to solve (2) for $F$; but one knows a more crude trial function $\varphi$—

$$\psi = \varphi + \Lambda = \psi_0 + \Delta, \qquad \Lambda \gg \Delta—$$

for which

$$[F_0, H]\varphi = \Omega\varphi - \frac{(\varphi, \Omega\varphi)}{(\varphi, \varphi)}\varphi$$

can be solved for $F_0$. The difference between $F_0$ and $F$ is easily seen to be of the order $\Lambda$, so that using $F_0$ in (1) instead of the correct $F$ but still using the accurate $\psi_0$ in (1) leaves an error in $[\Omega] - \langle\Omega\rangle$ of order of magnitude $(\Delta\Lambda)$ which is worse than the ideal $0(\Delta^2)$ (if we could find the exact $F$), but better than not using any $F$ at all: $0(\Delta)$.[1]

One final word about what energy is to be used for $\epsilon$ in (1). Since any constant may be added to $F$ and still leave (2) satisfied, it seems safest always to set $\epsilon = [E]$ so that in view of the identity

$$(\psi_0, (H_0 - [E])\psi_0) = 0$$

any constant added to $F$ will not affect the answer.

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[1] One can iterate this procedure to get even better accuracy. Set $F_0 = F_{00} + F_{01}$ where $F_{00}$ is defined as is $F_0$ above. Then solving for $F_{01}$ from

$$[F_{01}, H]\varphi = (\Omega - (\varphi, \Omega\varphi) - [F_{00}, H])\psi_0$$

one will have residual errors of order $\Delta\Lambda^2$ and $\Delta^2$. We have not found any examples where this technique was applicable.

## II. EXAMPLES BASED ON THE 2-ELECTRON ATOM

The Hamiltonian for 2-electrons in an atom of nuclear charge $Ze$ is

$$H = -\frac{\hbar^2}{2m}(\nabla_1{}^2 + \nabla_2{}^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}},$$

and we shall use the simple trial function for the ground state (spin singlet)

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

where

$$a = \frac{a_0}{Z - \frac{5}{16}}, \qquad a_0 = \frac{\hbar^2}{me^2}.$$

The Ritz energy is

$$[E] = -2\left(Z - \frac{5}{16}\right)^2 \frac{e^2}{2a_0}$$

and we can write

$$(H - [E])\psi_0 = \left(\frac{e^2}{r_{12}} - \frac{5}{16}\frac{e^2}{r_1} - \frac{5}{16}\frac{e^2}{r_2}\right)\psi_0 .$$

Since $[E]$ differs from the true energy $E$ by about 2 percent (for $Z = 2$) we expect that $\psi_0$ errs by $\sim \sqrt{2\%} \sim 14$ percent. We shall now calculate the expectation values of a few simple operators using (1) and see that we do come within about 2 percent (and not $\sim 14$ percent) of the values previously obtained with much more elaborate trial functions.

$\Omega = r_1{}^2 + r_2{}^2$ is the operator whose expectation value gives the value for the atomic diamagnetism. The appropriate $F$ equation is easily solved

$$F = \frac{2m}{\hbar^2}\left[-\frac{a}{6}(r_1{}^3 + r_2{}^3) - \frac{a^2}{2}(r_1{}^2 + r_2{}^2)\right].$$

We then have

$$(\psi_0, \Omega\psi_0) = 6a^2$$

as the zeroth order expectation value; and the first-order correction works out to be

$$2(\psi_0, F(H - [E])\psi_0) = 6a^2\frac{a}{a_0}\frac{31}{192},$$

which is an increase by

$$\sim\frac{16}{Z - \frac{5}{16}}\ \%.$$

For helium ($Z = 2$) we have

$$\left[\frac{r_1^2 + r_2^2}{a_0^2}\right] = 6\left(\frac{16}{27}\right)^2 \{1 + 0.096\} = 2.31,$$

which agrees with the first calculation of Slater (2), and is 3 percent smaller than the more elaborate result of Wikner and Das (3) or equivalently the Hartree result (4). The experimental value is variously quoted at 2.37 (4) and 2.44 (5).[2]

$\Omega = 1/r_1 + 1/r_2$ gives the diamagnetic shielding (of the nucleus by the electrons).

We find

$$(\psi_0, \Omega\psi_0) = \frac{2}{a}, \qquad F = \frac{2m}{\hbar^2}\frac{1}{2}(r_1 + r_2), \qquad 2(\psi_0, (H - [E])F\psi_0) = 0.$$

Thus for helium

$$\left[\frac{a_0}{r_1} + \frac{a_0}{r_2}\right] = 2\left(2 - \frac{5}{16}\right) = 3.375.$$

Hylleraas (6), using a six-parameter function gets 3.3764, and he found values very close to 3.375 for all the approximate wave functions he tried. It appears that $\langle 1/r_1 + 1/r_2 \rangle$ is very closely related to $\langle H \rangle$; and this is evidenced in our calculation by the vanishing of the first-order correction.

$\Omega = \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)$ is an extreme example since it measures the electron density at a point, and turns out to be quite sensitive to the correlation in the wave function. Its expectation value enters in the calculation of part of the relativistic energy level correction.

$$(\psi_0, \Omega\psi_0) = \frac{8}{a^3},$$

and we already know (1)

$$F = \frac{2m}{\hbar^2}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{2}{a}\ln r_1 r_2 + 2\frac{r_1 + r_2}{a}\right).$$

We find

$$2(\psi_0, F(H - [E])\psi_0) = \frac{8}{a^3}\frac{1}{(Z - 5/16)}\left(\frac{3}{2}\ln 2 - \frac{11}{16}\right).$$

Thus for He

$$4\pi a_0^3[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)] = (27/8)^3\{1 + (8/9 \ln 2 - 11/27)\}$$
$$= 38.4\{1 + .209\} = 46.4. \tag{3}$$

[2] We have calculated $\langle r^2 \rangle$ using the elaborate helium wave functions of Kinoshita (7) and get the value 2.37 $a_0^2$.

Here we have an excellent example of the improvement wrought by our techniques. The first-order correction is 21 percent and gives an answer within 2 percent of the value 45.5 given by Kinoshita (7).

### III. EXTENSION TO SECOND-ORDER PERTURBATIONS

Suppose we needed to calculate the second-order energy perturbation $E^{(2)}$ due to some operator $\Omega$ if, for example, the first-order $\langle \Omega \rangle$ vanished by reasons of symmetry.

$$E^{(2)} = \sum_n{}' \frac{\langle 0 \mid \Omega \mid n \rangle \langle n \mid \Omega \mid 0 \rangle}{E_0 - E_n}.$$

Here the states $\mid n \rangle$ and energies $E_n$ follow from the complete Hamiltonian of the unperturbed system $H$. According to the discussions of the preceding paper (1), we may set

$$E^{(2)} = (\psi, \Omega F \psi),$$

where $F$ is determined by $[F, H]\psi = \Omega\psi$ and we assume $(\psi, \Omega\psi) = 0$.

The problem is, If we cannot even solve exactly for $\psi$, one eigenstate of $H$, can we get an accurate evaluation of $E^{(2)}$?

The solution we give is the extension of what we have already done, i.e., we do effectively third-order perturbation theory starting with an approximation to $\psi$.

The following result can be proved by an analysis similar to that following Eq. (1). We define an approximation to $E^{(2)}$, $[E^{(2)}]$ calculated with some approximate wave function $\psi_0$

$$\begin{aligned}[E^{(2)}] = (\psi_0 \mid \Omega F_0 + G(H - \epsilon) + (H - \epsilon)G \\ + \tfrac{1}{2}F_0^2(H - \epsilon) + \tfrac{1}{2}(H - \epsilon)F_0^2 \mid \psi_0).\end{aligned} \tag{4}$$

Then it is claimed that $[E^{(2)}] \approx E^{(2)}$, i.e., we err only by terms of second order in $\psi - \psi_0$ if $F_0$ and $G$ are determined by the equations

$$[F_0, H]\psi_0 = \Omega\psi_0, \qquad [G, H]\psi_0 = \Omega F_0\psi_0 - \frac{(\psi_0, \Omega F_0\psi_0)}{(\psi_0, \psi_0)} \psi_0. \tag{5}$$

Using our earlier model of $\psi_0$ for the two-electron atom we now calculate the dipole polarizability:

$$\Omega = e\mathcal{E}[r_1 P_1(\cos \theta_1) + r_2 P_1(\cos \theta_2)].$$

We have from earlier work (1)

$$F_0 = \frac{2m}{\hbar^2} e\mathcal{E} \left[ P_1(\cos \theta_1) \left( -\frac{r_1 a^2}{2} - \frac{r_1^2 a}{4} \right) + P_1(\cos \theta_2) \left( -\frac{r_2 a^2}{2} - \frac{r_2^2 a}{4} \right) \right]$$

### TABLE I
#### POLARIZABILITIES OF 2-ELECTRON ATOMS [$\alpha$ IN UNITS OF (ANGSTROM)$^3$]

|         | Present work | Wikner and Das (3) | Sternheimer (8) | "Exp." (8)[a] |
|---------|--------------|--------------------|-----------------|---------------|
| H$^-$   | 7.60         | 14.88              | 13.4            | —             |
| He      | 0.183        | 0.218              | 0.224           | 0.204         |
| Li$^+$  | 0.0273       | 0.0305             | 0.0307          | 0.0235        |
| Be$^{++}$ | 0.00758    | 0.00813            | 0.00825         | 0.0059        |
| B$^{+++}$ | 0.00287    | 0.00303            | 0.00306         | 0.0029        |

[a] Of the values labeled "experimental" only that for He is reliable.

so the zeroth order result is

$$(\psi_0 , \Omega F_0 \psi_0) = -\frac{9}{2}\frac{a^4}{a_0}\mathcal{E}^2.$$

We find the solution of the equation for $G$ (by trial and error method):

$$G = \frac{4}{3}\mathcal{E}^2 \frac{1}{a_0} [g(r_1) + g(r_2) + P_1 (\cos \theta_{12})\mathcal{G}(r_1 , r_2)],$$

$$g(r) = \tfrac{9}{16}a^4 r^2 + \tfrac{3}{16}a^3 r^3 + \tfrac{1}{32}a^2 r^4,$$

$$\mathcal{G}(r_1 , r_2) = \frac{a^4}{4} r_1 r_2 + \frac{a^3}{8} (r_1 r_2^2 + r_2 r_1^2) + \frac{a^2}{16} r_1^2 r_2^2.$$

And we get the first-order correction in $[E^{(2)}]$

$$-\frac{9}{2}\frac{a^4}{a_0}\mathcal{E}^2 \frac{3}{16}\frac{a}{a_0} .$$

Setting $E^{(2)} = -\frac{1}{2}\alpha\mathcal{E}^2$ we have our evaluation of the polarizability $\alpha$

$$\alpha = \frac{9a_0^3}{(Z - \frac{5}{16})^4} \left\{ 1 + \frac{3}{16} \frac{1}{(Z - \frac{5}{16})} \right\}.$$

Numerical values in Table I compare fairly well with the results of more elaborate works.

### TABLE II
#### QUADRUPOLE SHIELDING FACTORS $\gamma_\infty$

|          | Present work | Das and Bersohn (10) |
|----------|--------------|----------------------|
| H$^-$    | 1.080        | 1.141                |
| He       | 0.413        | 0.416                |
| Li$^+$   | 0.255        | 0.256                |
| Be$^{++}$  | 0.185      | 0.185                |
| B$^{+++}$  | 0.144      | 0.145                |

We have carried out an analogous calculation for the quadrupole shielding factor $\gamma_\infty$ (9) resulting from the mixed second-order perturbation calculation with electron interactions $r^2 P_2(\cos\theta)$ and $r^{-3} P_2(\cos\theta)$. Our result is

$$\gamma_\infty(1s^2) = \frac{\tfrac{2}{3}}{(Z - \tfrac{5}{16})}\left\{1 + \frac{1}{(Z - \tfrac{5}{16})}\left[\frac{7}{40} + \frac{3840\ln 2 - 2671}{96}\right]\right\}$$

$$= \frac{\tfrac{2}{3}}{(Z - \tfrac{5}{16})} + \frac{0.0520}{(Z - \tfrac{5}{16})^2}.$$

The comparison with the result of the more elaborate calculations by Das and Bersohn (10) shown in Table II is quite favorable.

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