

VARIATION METHOD

For a system with more than one electron, we can't solve the Schrödinger Eq. exactly. We must develop methods of approximation, such as

Variation Method
Perturbation Theory
Combination Variation/Perturbation

The Variation Method doesn't calculate a direct solution to the Schrödinger Eq.; Rather, it uses an approximate wavefunction (called a *trial function*) to get the best approximation to the property of interest, such as the energy. It is much easier to get an approximate wavefunction that will give a good approximation to the energy than to get the exact wavefunction. This procedure works because you can prove a theorem that the energy that is calculated using the trial function is always greater than or equal to the exact ground state energy. As the trial function gets better (i.e. closer to the exact wavefunction, whatever that may be), then the energy approaches the exact ground state energy from above, i.e. it is an upper bound to the exact ground state energy.

THEOREM: Given a system with Hamiltonian operator H , if ϕ is any normalized well-behaved function that satisfies the boundary conditions of the problem, then

$$\int \phi^* H \phi \, d\tau \geq E_0,$$

where E_0 is the true value of the lowest energy eigenvalue of H .

Proof: Let $I = \int \phi^* (H - E_0) \phi \, d\tau \geq 0$

$$\begin{aligned}
&= \int \phi^* H \phi \, d\tau - \int \phi^* E_0 \phi \, d\tau \\
&= \int \phi^* H \phi \, d\tau - E_0 \int \phi^* \phi \, d\tau \\
&= \int \phi^* H \phi \, d\tau - E_0, \text{ assuming } \phi \text{ is normalized.}
\end{aligned}$$

Show $I \geq 0$:

Let ψ_i & E_i be the true (exact) eigenfunctions & eigenvalues of H:

$$H \psi_i = E_i \psi_i.$$

Since the ψ_i are a complete set, we can expand the trial function in terms of the ψ_i :

$$\phi = \sum_k a_k \psi_k$$

As a result, ϕ satisfies the same boundary conditions as the ψ_i .
Then

$$I = \int \phi^* (H - E_0) \phi \, d\tau$$

becomes

$$\begin{aligned}
I &= \int \sum_k a_k^* \psi_k^* (H - E_0) \sum_j a_j \psi_j \, d\tau \\
&= \int \sum_k a_k^* \psi_k^* \sum_j (H - E_0) a_j \psi_j \, d\tau
\end{aligned}$$

$$\begin{aligned}
&= \int \sum_k a_k^* \psi_k^* \sum_j (E_j - E_0) a_j \psi_j d\tau, \text{ since } H \psi_j = E_j \psi_j \\
&= \sum_{k,j} a_k^* a_j (E_j - E_0) \int \psi_k^* \psi_j d\tau \\
&= \sum_{k,j} a_k^* a_j (E_j - E_0) \delta_{kj} \\
&= \sum_k a_k^* a_k (E_k - E_0) \\
&= \sum_k |a_k|^2 (E_k - E_0)
\end{aligned}$$

Since E_0 is the lowest energy eigenvalue, $(E_k - E_0) \geq 0$. Also $|a_k|^2 \geq 0$. So $I \geq 0$.

If ϕ is not normalized, the Variation Method can still be used, but the overlap integral must be calculated:

$$I = \int \phi^* H \phi d\tau - E_0 \int \phi^* \phi d\tau$$

And $\int \phi^* H \phi d\tau / \int \phi^* \phi d\tau \geq E_0$

There are many possible ϕ 's. The best ϕ is the one for which the variational integral ($\int \phi^* H \phi d\tau$ or $\int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$) is closest to E_0 . If we happen to choose $\phi = \psi_0$, then we will calculate E_0 from the variational integral. Note that it is possible to get a good approximation to E_0 using a poor ϕ .

Method of Approach:

(1) Guess a form for the trial function.

(2) Include several variable parameters

(3) “Optimize” the variation integral with respect to these parameters (i.e. Take the partial derivative of the variation integral with respect to each of the N variable parameters & set it equal to zero. This gives N eq. Solve each of the N eq. simultaneously. This gives the parameters that determine the best ϕ .)

(4) Use ϕ to calculate

$$\int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$$

to get the best energy.

EXAMPLES: First, let's use the Variation Method on some exactly solvable problems to see how well it does in calculating E_0 .

(1) Find the upper bound to the ground state energy of a particle in a box of length L. $V = 0$ inside the box & ∞ outside. $\psi = 0$ outside the box. $H = -\hbar^2/(2m) d^2/dx^2$

Boundary Conditions: $\psi = 0, x = 0, L$

Trial function: $\phi = x(L-x)$ $0 \leq x \leq L$

$\phi = 0$ $x > L, x < 0$

Calculate $\int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$

$$\int \phi^* H \phi d\tau = \int_0^L [x(L-x)]^* [-\hbar^2/(2m) d^2/dx^2] [x(L-x)] dx$$

$$d/dx [x(L-x)] = L-x + x(-1)$$

$$d^2/dx^2 [x(L-x)] = -1 -1 = -2$$

$$\int \phi^* H \phi d\tau = \int_0^L [x(L-x)] [-\hbar^2/(2m)](-2) dx$$

$$= \hbar^2/m \int_0^L (xL - x^2) dx$$

$$= \hbar^2/m \{ L \int_0^L x dx - \int_0^L x^2 dx \}$$

$$= \hbar^2/m \{ L (L^2/2) - L^3/3 \}$$

$$= \hbar^2 L^3/(6m)$$

$$\int \phi^* \phi d\tau = \int_0^L [x(L-x)]^* [x(L-x)] dx$$

$$= \int_0^L x^2(L-x)^2 dx$$

$$= L^2 \int_0^L x dx + \int_0^L x^4 dx - 2L \int_0^L x^3 dx$$

$$= L^2(L^3/3) + L^5/5 - 2L(L^4/4)$$

$$= L^5/30$$

$$I = \int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$$

$$= \{ \hbar^2 L^3/(6m) \} / \{ L^5/30 \}$$

$$= 5 \frac{\hbar^2}{L^2 m^2} = 5 \frac{\hbar^2}{(4\pi^2 L^2 m^2)} = E \text{ (variational energy)}$$

By exact solution (Chapter 2), we found $E_0 = \frac{\hbar^2}{8L^2 m^2}$

$$\% \text{ error} = \left| \frac{E - E_0}{E_0} \right| \times 100$$

$$= \left| \frac{5 \frac{\hbar^2}{(4\pi^2 L^2 m^2)} - \frac{\hbar^2}{(8L^2 m^2)}}{\frac{\hbar^2}{(8L^2 m^2)}} \right| \times 100$$

$$= (5/\pi^2 - 1/2) \times 100$$

$$= 1.3\%$$

(2) One-Dimensional Harmonic Oscillator

Boundary Conditions: $\psi = 0, x = \pm\infty$

Find a form for the trial wavefunction that satisfies the boundary conditions:

$$e^{-x} \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$e^{-x} \rightarrow \infty \text{ as } x \rightarrow -\infty$$

$$e^{-x^2} \rightarrow 0 \text{ as } x \rightarrow \pm\infty$$

But since we can expand e^{-x^2} in a power series, the power to which e is raised must be dimensionless otherwise we will get terms in $(\text{Length})^2$, $(\text{Length})^4$, etc. in the expansion. So include a factor of

$$\alpha = 2\pi v m / \hbar \quad \text{units of } (\text{Length})^{-2}$$

Then αx^2 is dimensionless. Here, α is a constant, not a variable parameter.

Since $V = kx^2/2$ is an even function, we need a trial function that has a definite parity because the true wavefunction must be even or odd.

$(1 + b x^2) e^{-\alpha x^2}$ doesn't have a definite parity, but

$\phi = (1 + c \alpha x^2) e^{-\alpha x^2}$ does (even)

$$\begin{aligned} \int \phi^* \phi d\tau &= \int_0^\infty (1 + c \alpha x^2)^2 e^{-2\alpha x^2} dx \\ &= 2 \left\{ \int_0^\infty e^{-2\alpha x^2} dx + 2c\alpha \int_0^\infty x^2 e^{-2\alpha x^2} dx \right. \\ &\quad \left. + c^2 \alpha^2 \int_0^\infty x^4 e^{-2\alpha x^2} dx \right\} \\ &= 2 \left\{ (1/2) [\pi/(2\alpha)]^{1/2} + 2c\alpha/4 \right\} [\pi/(2\alpha)^3]^{1/2} \\ &\quad + c^2 \alpha^2 (3/8) [\pi/(2\alpha)^5]^{1/2} \\ &= [\pi/(2\alpha)]^{1/2} \{ 1 + c/2 + c^2 3/16 \} \end{aligned}$$

$$\int \phi^* H \phi d\tau = \frac{\hbar^2}{m} (\pi\alpha/2)^{1/2} \{ 43c^2/128 - c/16 + 5/8 \} \text{ (check on your own)}$$

$$I = \int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$$

$$= \frac{\hbar^2}{m(\pi\alpha/2)^{1/2}} \{43c^2/128 - c/16 + 5/8\} / [\pi/(2\alpha)]^{1/2} \{1 + c/2 + c^2/16\}$$

$$= \frac{\hbar^2\alpha}{(m8)} \{43c^2 - 8c + 80\} / \{16 + 8c + 3c^2\}$$

$$\partial I / \partial c = 0 \rightarrow \partial / \partial c \{43c^2 - 8c + 80\} / \{16 + 8c + 3c^2\} = 0$$

$$= (86c - 8)(16 + 8c + 3c^2) - \{43c^2 - 8c + 80\}(8 + 6c) / \{16 + 8c + 3c^2\}$$

This will be zero if the numerator = 0. Simplifying the numerator \rightarrow

$$23c^2 + 56c - 48 = 0 \quad \text{or } c = -3.107 \text{ or } 0.6718$$

Evaluate I with these two c 's to see which one gives the lower energy:

$$I = \frac{\hbar^2\alpha}{(m8)} \{43c^2 - 8c + 80\} / \{16 + 8c + 3c^2\}$$

and

$$\alpha = 2\pi vm / \hbar$$

$$\text{gives } I = E = hv \{43c^2 - 8c + 80\} / \{24c^2 + 64c + 128\}$$

$$c = 0.6718 \rightarrow \text{lower } E = 0.517hv$$

$$\text{Since } E_0 = 0.5 hv, \% \text{Error} = 3.4 \%$$

An alternative trial function could be

$$\phi = e^{-b\alpha x^{**2}}$$

Optimization of the variational integral gives $b=1/2$ & $E = 0.5$
 $h\nu = E_0$ (see homework problem). So in this case we happened
to have chosen a form for the trial function which is the ground
state wavefunction of the system.

Linear Variation Functions

A common type of trial function for the wavefunction of
molecules is one that contains the parameters as multiplicative
factors of functions rather than appearing in the exponents. The
trial function can be a linear combination of linearly
independent functions:

$$\phi = \sum_{i=1}^N c_i f_i$$

where the f_i satisfy the boundary conditions of the problem.

$$\begin{aligned} \text{So } \int \phi^* \phi \, d\tau &= \int \left(\sum_{i=1}^N c_i f_i \right)^* \left(\sum_{j=1}^N c_j f_j \right) \, d\tau \\ &= \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j \int f_i^* f_j \, d\tau \\ &= \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j S_{ij} \end{aligned}$$

where S_{ij} is the overlap integral, $\int f_i^* f_j \, d\tau$. $S_{ij} = 0$ only when the
 f 's are orthogonal. The f 's are not necessarily the
eigenfunctions of any operator.

$$\int \phi^* H \phi \, d\tau = \int \left(\sum_{i=1}^N c_i f_i \right)^* H \left(\sum_{j=1}^N c_j f_j \right) \, d\tau$$

$$\begin{aligned}
&= \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j \int f_i^* H f_j d\tau \\
&= \sum_{i=1}^N \sum_{j=1}^N c_i^* c_j H_{ij}
\end{aligned}$$

where H_{ij} is the integral, $\int f_i^* H f_j d\tau$.

Find the c 's which minimize the variation integral

$$I = \int \phi^* H \phi d\tau / \int \phi^* \phi d\tau$$

$$I = \frac{\sum_{i=1}^N \sum_{j=1}^N c_i^* c_j H_{ij}}{\sum_{i=1}^N \sum_{j=1}^N c_i^* c_j S_{ij}}$$

Find the c 's such that $\partial I / \partial c_i = 0$, $i = 1, \dots, N$

Rewrite the expression for I as

$$I \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k S_{jk} \right\} = \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k H_{jk} \right\}$$

Take the partial derivative of each side with respect to c :

$$\begin{aligned} (\partial I / \partial c_i) \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k S_{jk} \right\} + I \partial / \partial c_i \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k S_{jk} \right\} \\ = \partial / \partial c_i \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k H_{jk} \right\} \end{aligned}$$

The first term on the left = 0, since the $(\partial I / \partial c_i) = 0$ by design. Consider the second term on the left:

$$\begin{aligned} \partial / \partial c_i \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k S_{jk} \right\} &= \sum_{j=1}^N \sum_{k=1}^N \partial / \partial c_i (c_j^* c_k) S_{jk} \\ &= \sum_{j=1}^N \sum_{k=1}^N (c_k \partial c_j^* / \partial c_i + c_j^* \partial c_k / \partial c_i) S_{jk} \end{aligned}$$

$\partial c_j^* / \partial c_i = 0$ unless $j = i$. So $\partial c_j^* / \partial c_i = \delta_{ji}$ & $\partial c_k / \partial c_i = \delta_{ki}$. So

$$\partial / \partial c_i \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k S_{jk} \right\} = \sum_{j=1}^N \sum_{k=1}^N (c_k \delta_{ji} + c_j^* \delta_{ki}) S_{jk}$$

$j=1 \ k=1$

$j=1 \ k=1$

$$\begin{aligned}
&= \sum_{k=1}^N c_k \left(\sum_{j=1}^N \delta_{ji} S_{jk} \right) + \sum_{j=1}^N c_j^* \left(\sum_{k=1}^N \delta_{ki} S_{jk} \right) \\
&= \sum_{k=1}^N c_k S_{ik} + \sum_{j=1}^N c_j^* S_{ji} \\
&= 2 \sum_{k=1}^N c_k S_{ik}
\end{aligned}$$

Similarly,

$$\partial/\partial c_i \left\{ \sum_{j=1}^N \sum_{k=1}^N c_j^* c_k H_{jk} \right\} = 2 \sum_{k=1}^N c_k H_{ik}$$

$$\text{So } 2 \sum_{k=1}^N c_k S_{ik} = 2 \sum_{k=1}^N c_k H_{ik}, \quad i = 1, \dots, N$$

Or

$$\sum_{k=1}^N c_k (H_{ik} - S_{ik} I) = 0$$

The c_k 's are the unknowns, the $(H_{ik} - S_{ik} I)$ are the coefficients.

For example, for $N = 2$, we have a set of linear homogeneous eq.:

$$(H_{11} - S_{11}I)c_1 + (H_{12} - S_{12}I)c_2 = 0$$

$$(H_{21} - S_{21}I)c_1 + (H_{22} - S_{22}I)c_2 = 0$$

There will be a nontrivial solution for the c 's if the determinant of coefficients equals zero:

$$\begin{vmatrix} (H_{11} - S_{11}I) & (H_{12} - S_{12}I) \\ (H_{21} - S_{21}I) & (H_{22} - S_{22}I) \end{vmatrix} = 0$$

Or $(H_{11} - S_{11}I)(H_{22} - S_{22}I) - (H_{21} - S_{21}I)(H_{12} - S_{12}I) = 0$

This gives a quadratic Eq. in I. Solving for I gives two roots, I_0 & I_1 . It is possible to show that I_0 is an upper bound to E_0 , the exact ground state energy & that I_1 is an upper bound to E_1 , the exact energy of the first excited state. It can be shown that the number of states that are approximated depend on the number of terms in the trial function & that including more terms in the trial function does not change the accuracy of the previously-calculated energies.

For the general case with an N-term trial function, we must solve an NxN determinant

$$\begin{vmatrix} (H_{11} - S_{11}I) & \dots\dots & (H_{1N} - S_{1N}I) \\ \dots\dots & \dots\dots & \dots\dots\dots \\ (H_{N1} - S_{N1}I) & \dots\dots & (H_{NN} - S_{NN}I) \end{vmatrix} = 0$$

There will be N roots such that $I_0 \leq I_1 \dots \leq I_N$ & $E_0 \leq I_0, E_1 \leq I_1, \dots, E_N \leq I_N$

This is called the *Secular Eq.* and can be solved by the methods for solving homogeneous eq. The solution is made easier if the f's are chosen (or made) orthogonal. Then all the overlap integrals (S_{ij}) are zero.

After solving the Secular Eq. for the I 's, we can get ψ by first finding the c 's. Procedure to find E_0 & ψ_0 (example- $N=2$):

(1) Calculate I_0 from the secular eq. It will be the lowest root of

$$(H_{11} - S_{11}I) (H_{22} - S_{22}I) - (H_{21} - S_{21}I) (H_{12} - S_{12}I) = 0$$

(2) Use I_0 in the set of simultaneous Eq. to find the c_k 's:

$$\sum_{k=1}^N c_k (H_{ik} - S_{ik} I) = 0$$

For $N=2$:

$$(H_{11} - S_{11}I_0)c_1 + (H_{12} - S_{12}I_0)c_2 = 0$$

$$(H_{21} - S_{21}I_0)c_1 + (H_{22} - S_{22}I_0)c_2 = 0$$

Discard one of the eq. & solve for c_2 in terms of c_1 :

$$c_2 = c_1 (H_{11} - S_{11}I_0) / (H_{12} - S_{12}I_0)$$

(3) Find c_1 by normalization of ψ_0 . Calculate c_2 from c_1 .

EXAMPLE: Polarizability of H

The H atom is put into an electric field of strength F (a.u.) in the z -direction.

Let $\phi = c_1\phi_{1s} + c_2\phi_{2p}$,

where ϕ_{1s} & ϕ_{2p} are the exact 1s & 2p H atom wavefunctions. To simplify the calculations work in atomic units (a.u.). The unit of length is the Bohr radius and this is taken as 1. So

$$a_0 = \hbar^2 / (m_e e^2) = 1$$

Then $\phi_{1s} = 1/\sqrt{\pi} Z^{3/2} e^{-Zr}$ & $\phi_{2pz} = 1/[4\sqrt{(2\pi)}] Z^{5/2} e^{-Zr/2} \cos \theta$

$$\& H = -1/2 \nabla^2 - 1/r - F r \cos \theta = H_{\text{atom}} - F r \cos \theta,$$

$$E_N = -1/(2N^2)$$

where $z = r \cos \theta$.

Solve for I from:

$$\begin{vmatrix} (H_{11} - S_{11}I) & (H_{12} - S_{12}I) \\ (H_{21} - S_{21}I) & (H_{22} - S_{22}I) \end{vmatrix} = 0$$

$$\text{Or } (H_{11} - S_{11}I)(H_{22} - S_{22}I) - (H_{21} - S_{21}I)(H_{12} - S_{12}I) = 0$$

where $H_{11} = \langle \phi_{1s} | H | \phi_{1s} \rangle$

$$H_{12} = \langle \phi_{1s} | H | \phi_{2pz} \rangle$$

$$H_{21} = \langle \phi_{2pz} | H | \phi_{1s} \rangle$$

$$H_{22} = \langle \phi_{2pz} | H | \phi_{2pz} \rangle$$

$$S_{11} = \langle \phi_{1s} | \phi_{1s} \rangle = 1 \text{ since } \phi_{1s} \text{ is normalized}$$

$$S_{12} = \langle \phi_{1s} | \phi_{2pz} \rangle = 0 = S_{21} \text{ since } \phi_{1s} \text{ \& } \phi_{2pz} \text{ are orthogonal}$$

$$S_{22} = \langle \phi_{2pz} | \phi_{2pz} \rangle = 1 \text{ since } \phi_{2pz} \text{ is normalized}$$

$$\begin{aligned} H_{11} &= \langle \phi_{1s} | H | \phi_{1s} \rangle \\ &= \langle \phi_{1s} | H_{\text{atom}} | \phi_{1s} \rangle + \langle \phi_{1s} | -F r \cos \theta | \phi_{1s} \rangle \\ &= \langle \phi_{1s} | E_1 | \phi_{1s} \rangle + 0 = E_1 = -1/2 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} H_{22} &= \langle \phi_{2pz} | H | \phi_{2pz} \rangle \\ &= \langle \phi_{2pz} | H_{\text{atom}} | \phi_{2pz} \rangle + \langle \phi_{2pz} | -F r \cos \theta | \phi_{2pz} \rangle \\ &= \langle \phi_{2pz} | E_2 | \phi_{2pz} \rangle + 0 = E_2 = -1/8 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} H_{12} &= \langle \phi_{1s} | H | \phi_{2pz} \rangle \\ &= \langle \phi_{1s} | H_{\text{atom}} | \phi_{2pz} \rangle + \langle \phi_{1s} | -F r \cos \theta | \phi_{2pz} \rangle \\ &= E_2 \langle \phi_{1s} | \phi_{2pz} \rangle - 2^{15/2} F/3^5 \text{ a.u.} \\ &= -2^{15/2} F/3^5 \text{ a.u. since } \langle \phi_{1s} | \phi_{2pz} \rangle = 0 \end{aligned}$$

$$\begin{aligned} H_{21} &= \langle \phi_{2pz} | H | \phi_{1s} \rangle \\ &= \langle \phi_{2pz} | H_{\text{atom}} | \phi_{1s} \rangle + \langle \phi_{2pz} | -F r \cos \theta | \phi_{1s} \rangle \\ &= E_1 \langle \phi_{2pz} | \phi_{1s} \rangle - 2^{15/2} F/3^5 \text{ a.u.} \end{aligned}$$

$$= -2^{15/2} F/3^5 \text{ a.u. since } \langle \phi_{2pz} | \phi_{1s} \rangle = 0$$

So solving the determinant for I gives

$$(-1/2 - I) (-1/8 - I) - (-2^{15/2} F/3^5) (-2^{15/2} F/3^5) = 0$$

$$I = -5/16 \pm (9/64 + 2^{17}F^2/3^{10})^{1/2}/2$$

If $F=0$, get $I = E = -1/2$ or $-1/8$ (the exact 1s & 2p energies)

If $F = 0.1$ a.u., $I = -0.51425$ a.u. & -0.1107 a.u.; $E_0 = -0.51425$ a.u. is the best upper bound to the 1s state energy (-0.5 a.u.).

Find c_1 & c_2 & for $F = 0.1$ a.u. & $E_0 = -0.51425$ a.u.:

$$c_1 (H_{11} - E_0) + c_2 (H_{12}) = 0$$

$$c_1 (H_{12}) + c_2 (H_{22} - E_0) = 0$$

Substituting gives

$$0.01425 c_1 - 0.074493 c_2 = 0$$

$$- 0.074493 c_1 + 0.38925 c_2 = 0$$

Dropping the second eq. & solving for c_1 from the first gives

$$c_1 = 5.227 c_2$$

Normalizing the wavefunction gives

$$|c_1|^2 + |c_2|^2 = 1$$

$$(5.227 c_2)^2 + c_2^2 = 1 \rightarrow c_2 = \pm 0.18789$$

If $c_2 = + 0.18789$, $c_1 = 0.98219$. (the choice of the positive root for c_2 is arbitrary). then

$$\phi = 0.98219 \phi_{1s} + 0.18789 \phi_{2pz}$$

Note that most of the contribution comes from ϕ_{1s} , which agrees with the fact that the variational energy is an upper bound to the ground state energy.

If we used the other root of the eq., $I = -0.1107$, then

$$\phi = -0.18789 \phi_{1s} + 0.98219 \phi_{2pz}$$

and this is an upper bound to the first excited state (n=2 level). However, it may not be a good approximation since there is no ϕ_{2s} component.