

8.2: An aside: Variational Theory, another approximation method

= an approximation method which works even when perturbation theory fails.
Especially useful and important for many-electron systems.

Theorem: $\tilde{E} = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle \geq E_0$

\tilde{E} Approximate energy of the system

$\tilde{\psi}$ “any” normalized function of the coordinates of the system including spin.
= trial wave function which must satisfy the usual QM boundary conditions.

E_0 Lowest energy eigenvalue for the system (ground state)

Proof:



Derivation ahead



(1) Set $\tilde{\psi} = \psi_o$ = exact ground state wave function.

$$\Rightarrow \tilde{E} = \langle \psi_o | \hat{H} | \psi_o \rangle = E_o \langle \psi_o | \psi_o \rangle = E_o$$

i.e. the theorem holds for $\tilde{\psi} = \psi_o$ exactly

(2) When $\tilde{\psi} \neq \psi_o$ which is usually the case

Will use our theorem that any arbitrary function can be expressed as an expansion in a complete basis set.

Use expansion postulate to expand $\tilde{\psi}$ in terms of a complete set of eigenfunctions of \mathbf{H} .

$$\Rightarrow \tilde{\psi} = \sum_{k=0}^{\infty} a_k \psi_k \quad \left[\begin{array}{l} \hat{H} \psi_k = E_k \psi_k; \langle \psi_l | \psi_k \rangle = \delta_{lk} \\ k = 0, 1, 2, \dots, \infty; E_o \leq E_1 \leq E_2 \dots \end{array} \right]$$

Of course, if we actually knew the exact wave functions of \mathbf{H} then we would not be dealing with any approximation method. However, this is a formality we need to prove the theorem.

Require $\tilde{\psi}$ to be normalized

$$\begin{aligned}
 \therefore 1 &= \langle \tilde{\psi} | \tilde{\psi} \rangle = \left\langle \sum_k a_k \psi_k \mid \sum_p a_p \psi_p \right\rangle \\
 &= \sum_k \sum_p a_k^* a_p \langle \psi_k | \psi_p \rangle = \sum_k \sum_p a_k^* a_p \delta_{kp} \\
 &\qquad\qquad\qquad = 0 \text{ if } p \neq k \\
 &\qquad\qquad\qquad = 1 \text{ if } p = k \\
 &= \sum_k a_k^* a_k = \sum_k |a_k|^2
 \end{aligned}$$

Then

$$\tilde{E} = \left\langle \tilde{\psi} \mid \hat{H} \mid \tilde{\psi} \right\rangle = \left\langle \sum_k a_k \psi_k \mid \hat{H} \mid \sum_p a_p \psi_p \right\rangle$$

$$\begin{aligned}
&= \sum_k \sum_p a_k^* a_p \langle \psi_k | \hat{H} | \psi_p \rangle = \sum_k \sum_p a_k^* a_p E_p \langle \psi_k | \psi_p \rangle \\
&= \sum_k \sum_p a_k^* a_p E_p \delta_{kp} = \sum_k |a_k|^2 E_k
\end{aligned}$$

Subtract E_o from both sides

$$\begin{aligned}
\tilde{E} - E_o &= \sum_{k=0}^{\infty} |a_k|^2 E_k - E_o = \sum_{k=0}^{\infty} |a_k|^2 E_k - E_o \sum_{k=0}^{\infty} |a_k|^2 \\
&= \sum_{k=0}^{\infty} |a_k|^2 (E_k - E_o)
\end{aligned}$$

$$\Rightarrow \tilde{E} - E_o \geq 0 \Rightarrow \tilde{E} \geq E_o$$

But $E_k \geq E_o$ for all k since E_o is the ground state energy. Note as well that $|a_k|^2 \geq 0$ for all k .

This theorem is the basis of the variational method for calculating approximate wave functions and energies of many electron atoms and molecules

Note: The theorem holds for the lowest energy state for each state of a given symmetry, if

$\tilde{\psi}$ is chosen to have the correct symmetry; for example, the lowest s state, p state, d state etc.

$$\Rightarrow \tilde{E} \geq E_{sym, \ell}$$

Variational Method

Start with $\hat{H} \tilde{\psi} = \tilde{E} \tilde{\psi}$

Premultiply by $\tilde{\psi}^*$ integrate, and rearrange for E

$$\Rightarrow E = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} \quad (1)$$

Let: $\tilde{\psi} = \sum_{i=1}^N c_i f_i$

where $\{f_i\}$ are functions that satisfy the general conditions for a wave function. They may constitute an orthonormal set or they may not.

$$\tilde{E} = \frac{\sum_{j=1}^N \sum_{i=1}^N c_j^* c_i \langle f_j | \hat{H} | f_i \rangle}{\sum_{j=1}^N \sum_{i=1}^N c_j^* c_i \langle f_j | f_i \rangle} = \frac{\sum_{j=1}^N \sum_{i=1}^N c_j^* c_i H_{ji}}{\sum_{j=1}^N \sum_{i=1}^N c_j^* c_i S_{ji}} \quad (2)$$

where

$$H_{ji} = \langle f_j | \hat{H} | f_i \rangle \quad ; \quad S_{ji} = \langle f_j | f_i \rangle$$

H_{ji} is a Hamiltonian matrix element and S_{ji} is an overlap integral

Rearrange (2) such that

$$\tilde{E} \sum_{j=1}^N \sum_{i=1}^N c_j^* c_i S_{ji} = \sum_{j=1}^N \sum_{i=1}^N c_j^* c_i H_{ji} \quad (3)$$

We want coefficients $\{c\}$ that make E a minimum. We can do this by differentiating (3) with respect to c_k and setting

$$\frac{\partial E}{\partial c_k} = 0$$

Do the case for $i,j = 1,2$

$$\tilde{E}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

Differentiate with respect to c_1

$$\begin{aligned} & (2c_1 S_{11} + 2c_2 S_{12})E + (c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) \frac{\partial E}{\partial c_1} \\ & = 2c_1 H_{11} + 2c_2 H_{12} \end{aligned}$$

Similarly, differentiation with respect to c_2 yields:

$$\begin{aligned} & (2c_2 S_{22} + 2c_1 S_{12})E + (c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) \frac{\partial E}{\partial c_2} \\ & = 2c_2 H_{22} + 2c_1 H_{12} \end{aligned}$$

Set $\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$ and rearrange to show:

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

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

This will have non-trivial $\{c_i\}$ solutions if the following determinant = 0.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

= **SECULAR EQUATION** (like before)

For N basis functions, the secular equation is given by:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \dots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

The secular equation yields a N^{th} order polynomial in E. For each E can solve for $\{c_i\}$ to get the “best” approximate wave function for the system having that E.

Back to the problem:

8.3: Optimization of the Radial Part by the Variation Method

What function should we use for the individual **entries**, $\phi_i(k)$ in the determinant? Instead of the H-atom eigenfunctions, we use modified functions. The key difference in the modified functions from the H-atom functions

Effective nuclear charge Zeta (ζ) < the true nuclear charge

The outermost electrons are **shielded** from the full nuclear charge by other electrons. Each 1- e^- orbital is constructed from a linear combination of H-atom-like orbitals. All coefficients in the linear combination in each orbital are used as variational parameters. The ζ values are optimized separately.

Next: solve the Schrodinger Equation for each electron i . To do so, we must know V_i^{eff} . This means that we must know the functional forms of all the other orbitals, also the case for the remaining $n-1$ electrons. That is, the answers must be known to solve the problem.

The way out of this quandary is to use an iterative approach.

- Make a reasonable guess for an initial set of orbitals
- Calculate an effective potential using these orbitals
- Calculate the energy and orbital functions for each of the n electrons in turn
- New orbitals are used to refine the initial guesses

Repeat until the solutions for the energies and the orbitals are **self-consistent**