The variational principle

The main problem we will like to address by the end of this handout is some (numerical) means of solving efficiently the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

References

The material reviewed here is standard and can be found in any Quantum Mechanics textbook and in brief in several of the electronic structure calculations books.

Recommended reading material for these slides is given below:

- Principles of Quantum Mechanics, by R. Shankar
- Introduction to Quantum Mechanics, D. J. Griffiths
- Quantum Mechanics, B. H. Bransden and C.J. Joachain
- Methods of Electronic-Structure Calculations, M. Springborg

The variational principle

- We are looking for an approximate solution $\Phi \simeq \Psi$ to the Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

- More precisely we are looking (at the absolute zero temperature) for the ground state (lowest eigenvalue a_0 of the Hermitian operator $\hat{H}$)

$$a_0 \leq a_1 \leq a_2 \leq a_3 \leq \cdots \leq a_{n-1} \leq a_n \leq a_{n+1} \leq \cdots .$$

- Let the (orthonormal) eigenvectors of $\hat{H}$ be f_n

$$\langle f_n | f_m \rangle = \delta_{n,m}$$

- We emphasize that we don't know the eigenvectors f_n

- The expectation value for the operator $\hat{H}$ occupying the state f_0 is the following:

$$\frac{\langle f_0 | \hat{H} | f_0 \rangle}{\langle f_0 | f_0 \rangle} = \frac{\langle f_0 | a_0 | f_0 \rangle}{\langle f_0 | f_0 \rangle} = \frac{a_0 \langle f_0 | f_0 \rangle}{\langle f_0 | f_0 \rangle} = a_0$$

The variational principle

- What will happen to the expectation value $\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$ when we use an approximation ϕ of the eigenvector f_0 ?

- Using the completeness of the eigenvectors we can write:

$$\phi = \sum_n c_n f_n$$

- With substitution to the expectation value we compute:

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \hat{H} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle} = \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} \hat{H} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}$$

The variational principle

- or using the orthonormality of the eigenvectors

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} a_{n_2} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle} = \frac{\sum_{n_1,n_2} \langle c_{n_1} f_{n_1} | c_{n_2} a_{n_2} f_{n_2} \rangle}{\sum_{n_1,n_2} \langle c_{n_1} f_{n_1} | c_{n_2} f_{n_2} \rangle}$$

$$= \frac{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} a_{n_2} \langle f_{n_1} | f_{n_2} >}{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} \langle f_{n_1} | f_{n_2} \rangle} = \frac{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} a_{n_2} \delta_{n_1,n_2}}{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} \delta_{n_1,n_2}}$$

$$= \frac{\sum_n c_n^* c_n a_n}{\sum_n c_n^* c_n} = \frac{\sum_n |c_n|^2 a_n}{\sum_n |c_n|^2} \geq \frac{\sum_n |c_n|^2 a_0}{\sum_n |c_n|^2} = \frac{a_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = a_0$$

- Thus the expectation value is greater or equal to the ground state eigenvalue a_0

The variational principle

- The general procedure using the variational method is to write f_0 in terms of some unknown parameters and then minimize the expectation with respect to these parameters, i.e.

$$\phi = \phi(p_1, p_2, \ldots, p_{N_p}; \vec{x}).$$

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \equiv \tilde{a}(p_1, p_2, \ldots, p_{N_p}).$$

$$\frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_1} = \frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_2} = \cdots = \frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_{N_p}} = 0$$

- In general, this is not an efficient approach.

- Let us apply this approach for the single electron in the H-atom

The variational principle

- Using atomic units $\hbar = m = |e| = 4\pi\varepsilon_0 = 1$, the Hamiltonian takes the form:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

- We know from quantum mechanics that the ground state is the following:

$$\hat{H}\psi_n = e_n\psi_n \qquad e_0 = -\frac{1}{2} \qquad \psi = \frac{1}{\sqrt{\pi}}\mathrm{e}^{-r}$$

- Approximate the ground state as $\phi = \left(\frac{2\alpha}{\pi}\right)^{3/4}\mathrm{e}^{-\alpha r^2}$, which is a normalized Gaussian with one (unknown) parameter

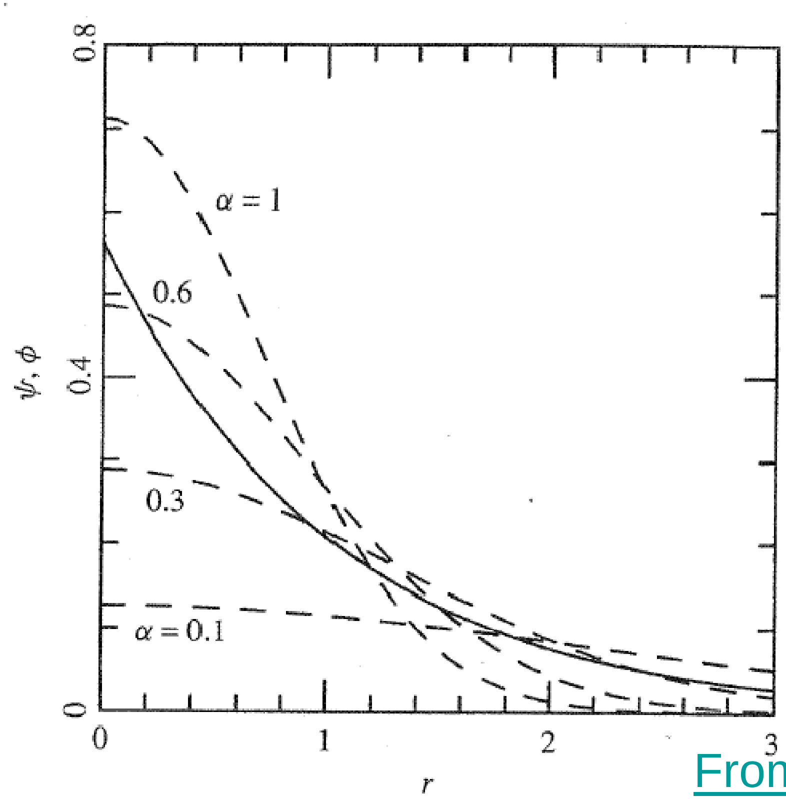
- Substituting this expression into the expectation value $\tilde{E}(\alpha) = \langle\phi|\hat{H}|\phi\rangle$ results in:

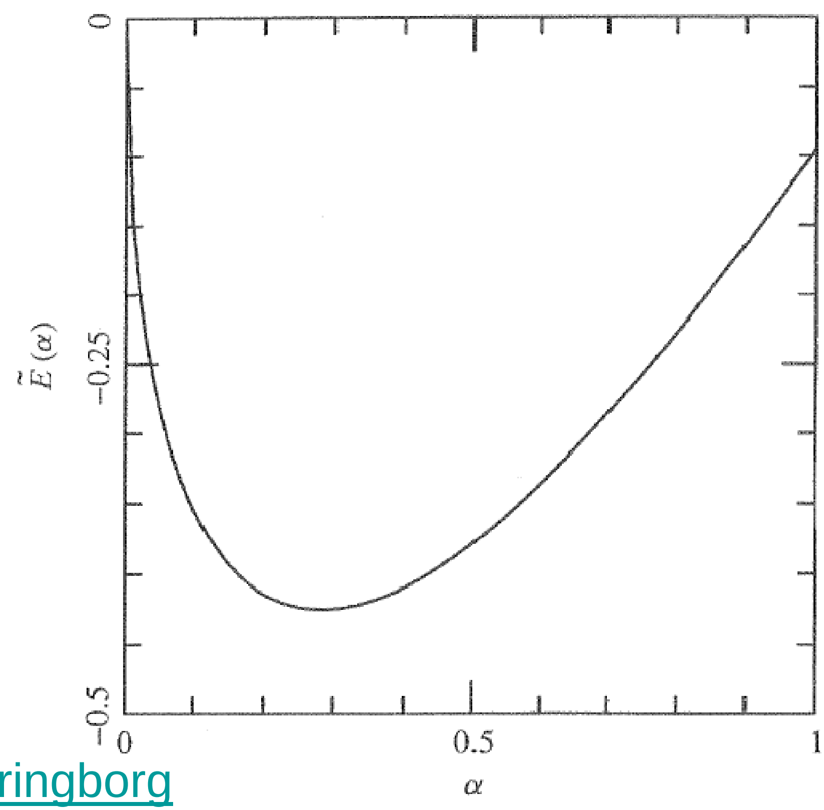
$$\tilde{E}(\alpha) = \frac{3\alpha}{2} - 2\left(\frac{2\alpha}{\pi}\right)^{1/2}$$

The variational principle

- Minimization with respect to the unknown parameter α, results in the following:

$$\alpha = \frac{8}{9\pi} \simeq 0.283 \qquad \tilde{E}\left(\alpha = \frac{8}{9\pi}\right) = -\frac{4}{3\pi} \simeq -0.424$$





From Springborg

The general form of the variational principle

- Let us approximate the ground state using a fixed basis with some coefficients:

$$\phi(\vec{x}) = \sum_{i=1}^{N_b} c_i \chi_i(\vec{x})$$

- Substitute in the expectation value and minimize it wrt to the coefficients c_k or for convenience wrt their complex conjugate values c_k^* !

$$\frac{\partial}{\partial c_k^*} \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = 0 \qquad k = 1, \ldots, N_b \quad \text{with the constraint} \quad \langle \phi | \phi \rangle = 1$$

- Using Lagrange multiplier λ, we can restate the problem as minimization of the function *K* wrt to λ and c_k^* as shown below:

$$K = \langle \phi | \hat{H} | \phi \rangle - \lambda [\langle \phi | \phi \rangle - 1] \qquad \Rightarrow \qquad \frac{\partial K}{\partial c_k^*} = \frac{\partial K}{\partial \lambda} = 0.$$

The general form of the variational principle

- The condition $\frac{\partial K}{\partial \lambda} = 0$ results in $\langle \phi | \phi \rangle = 1$
- The other condition $\frac{\partial K}{\partial c_k^*} = 0$, leads to the following:

$$\frac{\partial}{\partial c_k^*}\left[\left\langle \sum_i c_i \chi_i \middle| \hat{H} \middle| \sum_j c_j \chi_j \right\rangle - \lambda \left(\left\langle \sum_i c_i \chi_i \middle| \sum_j c_j \chi_j \right\rangle - 1 \right)\right]$$

$$= \frac{\partial}{\partial c_k^*}\left(\left\langle \sum_i c_i \chi_i \middle| \hat{H} \middle| \sum_j c_j \chi_j \right\rangle - \lambda \left\langle \sum_i c_i \chi_i \middle| \sum_j c_j \chi_j \right\rangle\right)$$

$$= \frac{\partial}{\partial c_k^*} \sum_{i,j} c_i^* c_j [\langle \chi_i | \hat{H} | \chi_j \rangle - \lambda \langle \chi_i | \chi_j \rangle]$$

$$= \sum_j c_j [\langle \chi_k | \hat{H} | \chi_j \rangle - \lambda \langle \chi_k | \chi_j \rangle] \equiv 0.$$

- From which we conclude: $\sum_j c_j \langle \chi_k | \hat{H} | \chi_j \rangle = \lambda \sum_j c_j \langle \chi_k | \chi_j \rangle, \quad k = 1, 2, \ldots, N_b.$

The general form of the variational principle

- The derived equation defines a generalized eigenvalue problem

$$\sum_j c_j \langle \chi_k | \hat{H} \chi_j \rangle = \lambda \sum_j c_j \langle \chi_k | \chi_j \rangle, \qquad k = 1, 2, \ldots, N_b.$$

$$\underline{\underline{A}}_{kj} = \langle \chi_k | \hat{H} | \chi_j \rangle \qquad \underline{\underline{O}}_{kj} = \langle \chi_k | \chi_j \rangle$$ Overlap matrix

$$\underline{\underline{A}} \cdot \underline{c} = \lambda \cdot \underline{\underline{O}} \cdot \underline{c}.$$

- Here the vector *c* contains all unknown coefficients (that may need to be normalized to enforce $\langle \phi | \phi \rangle = 1$)

- From the eigenvalue problem we compute N_b eigenvalues and we need to select the lowest.

An interesting property of the Lagrange multiplier approach

- An interesting property: The multiplier λ is the sought expectation value!

- Indeed, the sought expectation value is given as follows:

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_{i,j} c_i^* c_j \langle \chi_i | \hat{H} | \chi_j \rangle}{\sum_{i,j} c_i^* c_j \langle \chi_i | \chi_j \rangle}$$

- However, from the derived eigenvalue problem we can see that:

$$\sum_i c_j \langle \chi_k | \hat{H} | \chi_j \rangle = \lambda \sum_i c_j \langle \chi_k | \chi_j \rangle, \qquad \Rightarrow$$

$$\sum_{j,k} c_k^* c_j \langle \chi_k | \hat{H} | \chi_j \rangle = \lambda \sum_{j,k} c_k^* c_j \langle \chi_k | \chi_j \rangle$$

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- However, from the derived eigenvalue problem we can see that:

$$\sum_{j,k} c_k^* c_j \langle \chi_k | \hat{H} \chi_j \rangle = \lambda \sum_{j,k} c_k^* c_j \langle \chi_k | \chi_j \rangle \Rightarrow \lambda = \frac{\sum_{j,k} c_k^* c_j \langle \chi_k | \hat{H} | \chi_j \rangle}{\sum_{j,k} c_k^* c_j \langle \chi_k | \chi_j \rangle}$$