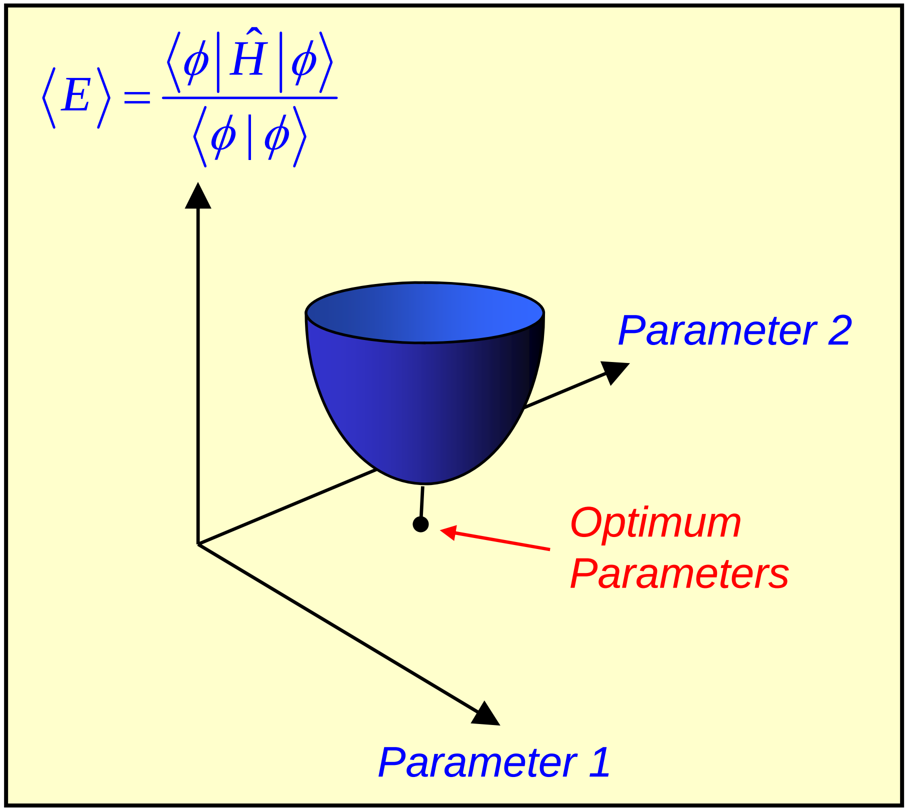
Advanced Quantum Physics

Lecture 5



David Ritchie

www.sp.phy.cam.ac.uk/~dar11/pdf

Section 2 – Methods of Approximation

- Very few problems in Quantum Mechanics can be solved analytically.
- For many situations we must resort to approximate techniques.

2.1 Variational methods: Ground state (1)

- Based on the completeness property of the set of eigenfunctions of the Hamiltonian:

$$\hat{H}\psi_j = E_j\psi_j$$

- Choose a trial wavefunction – $\phi(\mathrm{r})$ not necessarily normalised.
- Normalize it:

$$\phi'(\mathrm{r}) = \frac{\phi(\mathrm{r})}{\sqrt{\langle\phi\,|\,\phi\rangle}} \qquad \text{where} \quad \langle\phi\,|\,\phi\rangle \equiv \int |\,\phi(\mathbf{r})\,|^2\, d^3\mathbf{r}\,.$$

- Clearly $\phi(\mathrm{r})$ must be normalizable – the integral must converge
- Expectation value of energy of state $|\phi'\rangle$ is:

$$\langle E\rangle = \langle\phi'|\hat{H}|\phi'\rangle = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi\,|\,\phi\rangle}\,.$$

Ground state (2)

- Due to completeness of the set of eigenfunctions we can expand the trial wavefunction:

$$\phi(\mathbf{r}) = \sum_n c_n \psi_n(\mathbf{r}) \,,$$

$$\hat{H}\psi_n = E_n \psi_n$$

- Hence:

$$\langle \phi | \hat{H} | \phi \rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \hat{H} | \psi_n \rangle = \sum_{m,n} c_m^* c_n E_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 \; E_n$$

given orthonormality:

$$\langle \psi_m | \psi_n \rangle \equiv \int \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) d^3\mathbf{r} = \delta_{mn} \;.$$

- Similarly: $\langle \phi | \phi \rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 \,.$

- So

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2} \,.$$

Ground state (3)

- To estimate the energy of the ground state E_0:

Excited states have $E_n > E_0$ so $\sum_n E_n |c_n|^2 \geq E_0 \sum_n |c_n|^2$.

- Hence

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2} \geq E_0 .$$

- So by varying the arbitrary function $\phi(\mathbf{r})$ we can get an upper bound on the energy of the ground state.

- So… choose a function with one or more variable parameters.

(For example: a Gaussian, $\exp\left(-\alpha x^2\right)$ parameter α.)

- $\langle E \rangle$ is then a function of these parameters and can be minimized.

- If $\phi(\mathbf{r})$ is exactly the ground state wavefunction then $\langle E \rangle_{min} = E_0$ otherwise $\langle E \rangle_{min}$ is an upper bound on E_0 .

- Estimate is more precise as $\phi(\mathrm{r}) \rightarrow \psi_0(\mathrm{r})$ - so guess well!

Ground state (4)

- A good estimate of the ground state energy depends on an intelligent choice of wavefunction
- However a poor trial wavefunction can provide a better than expected estimate.
- Why? – because the discrepancy between $\langle E \rangle$ and E_0 is quadratic in the discrepancy between the trial wavefunction $\phi(\mathrm{r})$ and $\psi_0(\mathrm{r})$.
- To show this suppose that $\phi(\mathrm{r}) = \psi_0(\mathrm{r}) + \varepsilon\psi_k(\mathrm{r})$ where $|\psi_k\rangle$ is an excited state and ε is small.
- Since $\langle E \rangle = \dfrac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2}$ we can write:

$$\langle E \rangle = (E_0 + |\varepsilon|^2 E_k)/(1 + |\varepsilon|^2) \simeq E_0 + |\varepsilon|^2 (E_k - E_0)\,.$$

- Thus a 10% admixture of an excited state wavefunction leads to an increase in $\langle E \rangle$ of order 1%

Example – The Helium atom (1)

- To calculate the ground state energy of Helium
- Charge on nucleus Ze Two electrons with coordinates $\mathbf{r}_1, \mathbf{r}_2$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right) \quad \begin{cases} \nabla_1^2 \text{ w.r.t. } \mathrm{r}_1 \\ \nabla_2^2 \text{ w.r.t. } \mathrm{r}_2 \\ r_{12} = \left|\mathbf{r_1} - \mathbf{r_2}\right| \end{cases}$$

- To choose ϕ:
- In ground state expect both electrons in 1s level with opposite spins.
- 1s wavefunction similar to H atom – but nuclear charge screened from one electron by the other.
- Use

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{\frac{3}{2}} e^{-Z'r/a_0}, \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

- Overall wavefunction $\phi = \psi_{1s}(r_1)\psi_{1s}(r_2)$
- Z' as a free parameter (we expect $1 < Z' < 2$).

The Helium atom (2)

We calculate the energy expectation value for electron 1

$$R_\infty = \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{2a_0} = 13.6eV$$

- From solution of H atom:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Z'e^2}{4\pi\varepsilon_0 r_1}\right)\psi_{1s}(r_1) = -Z'^2 R_\infty \psi_{1s}(r_1)$$

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\right)\psi_{1s}(r_1) = -Z'^2 R_\infty \psi_{1s}(r_1) + \frac{Z'e^2}{4\pi\varepsilon_0 r_1}\psi_{1s}(r_1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}(r_1)$$

term added to both sides of eqn.

- Hence:

Energy for electron no.1 (from H atom)

$$\left\langle \phi \left| -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} \right| \phi \right\rangle = -Z'^2 R_\infty + \int \frac{(Z'-Z)e^2}{4\pi\varepsilon_0 r_1} \left|\psi_{1s}(r_1)\right|^2 d^3 r_1$$

- With $\psi_{1s}(r_1) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{\frac{3}{2}} e^{-Z'r_1/a_0}$ & using $\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{a^{n+1}}$ the integral gives:

$$\frac{e^2}{4\pi\varepsilon_0}\frac{(Z'-Z)Z'^3}{\pi a_0^3}\int_0^\infty 4\pi r_1^2 \frac{e^{-2Z'r_1/a_0}}{r_1} dr_1 = \frac{e^2}{4\pi\varepsilon_0 a_0} Z'(Z'-Z)$$

- So

$$\left\langle \phi \left| -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} \right| \phi \right\rangle = R_\infty\left[Z'^2 - 2ZZ'\right]$$

A similar result applies to the second electron

The Helium atom (3)

•The electrostatic interaction between the 2 electrons gives us:

$$\langle\phi|\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\phi\rangle = \frac{e^2}{4\pi\varepsilon_0}\iint|\psi_{1s}(r_1)|^2|\psi_{1s}(r_2)|^2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}d^3r_1d^3r_2$$

Since $d^3r = r^2 dr d\Omega$

$$=\left(\frac{1}{\pi}\frac{Z'^3}{a_0^3}\right)^2\frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r_1^2 e^{-2Z'r_1/a_0}dr_1\int_0^\infty r_2^2 e^{-2Z'r_1/a_0}dr_2\int d\Omega_1\int\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}d\Omega_2$$

•Now $\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\frac{1}{\sqrt{\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)}}$, θ is the angle between $\mathbf{r_1}$ and $\mathbf{r_2}$

•Choosing the direction of $\mathbf{r_1}$ as the z-axis we can write:

$$\int\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}d\Omega_2=\int_0^{2\pi}d\phi\int_{-1}^{1}\frac{1}{\sqrt{\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)}}d(\cos\theta)$$

$$=-\frac{2\pi}{r_1r_2}\left[\sqrt{\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)}\right]_{\cos\theta=-1}^{\cos\theta=1}=\frac{2\pi}{r_1r_2}\left(r_1+r_2-|r_1-r_2|\right)$$

where the integral over ϕ yields a factor of 2π

The Helium atom (4)

- The integral over Ω_1 yields a factor of 4π so overall:

$$\left\langle \phi \right| \frac{e^2}{4\pi\varepsilon_0 r_{12}} \left| \phi \right\rangle = \left(\frac{Z'}{a_0}\right)^6 \frac{8e^2}{4\pi\varepsilon_0} \int_0^\infty r_1^2 e^{-2Z'r_1/a_0} dr_1 \int_0^\infty r_2^2 e^{-2Z'r_2/a_0} dr_2 \frac{1}{r_1 r_2}\left(r_1 + r_2 - \left|r_1 - r_2\right|\right)$$

$$= \left(\frac{Z'}{a_0}\right)^6 \frac{8e^2}{4\pi\varepsilon_0} \int_0^\infty r_1 e^{-2Z'r_1/a_0} dr_1 \left\{ 2\int_0^{r_1} r_2^2 e^{-2Z'r_2/a_0} dr_2 + 2r_1 \int_{r_1}^\infty r_2 e^{-2Z'r_2/a_0} dr_2 \right\}$$

- Using standard integrals we get: $\left\langle \phi \right| \frac{e^2}{4\pi\varepsilon_0 r_{12}} \left| \phi \right\rangle = \frac{5}{4} Z' R_\infty$

- Adding the terms together: $\left\langle \phi \right| \hat{H} \left| \phi \right\rangle = R_\infty \left[2Z'^2 - 4ZZ' + \frac{5}{4} Z' \right]$
- Minimize w.r.t. Z' Gives $4Z' - 4Z + \frac{5}{4} = 0 \Rightarrow Z' = Z - \frac{5}{16} = \frac{27}{16}$
- If e-e interaction is absent then we get $Z' = Z$ as expected
- So $\left\langle \phi \right| \hat{H} \left| \phi \right\rangle = -2\left(\frac{27}{16}\right)^2 R_\infty = -77.4 eV$ (c/w experimental value $-79.0 eV$)
- A reasonable result – could refine estimate using a more complicated trial function (and a computer….)

The Rayleigh-Ritz Method

•A slightly different approach, take a trial function of the form:

$$\phi(\mathrm{r}) = \sum_j \alpha_j \psi_j(\mathrm{r})$$

•$\psi_j(\mathrm{r})$ are a linearly independent set of functions (not necessarily complete or ortho-normal).Coefficients α_j are variational parameters.

•So:

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_{j,k} \alpha_j \alpha_k \langle \psi_j | \hat{H} | \psi_k \rangle}{\sum_{j,k} \alpha_j \alpha_k \langle \psi_j | \psi_k \rangle} \equiv \frac{\sum_{j,k} \alpha_j \alpha_k H_{jk}}{\sum_{j,k} \alpha_j \alpha_k S_{jk}}$$

• H_{jk} are matrix elements of Hamiltonian, S_{jk} 'overlap' integrals. Minimizing w.r.t α_i:

$$0 = \sum_j \alpha_j H_{ij} \sum_{j,k} \alpha_j \alpha_k S_{jk} - \sum_{j,k} \alpha_j \alpha_k H_{jk} \sum_j \alpha_j S_{ij}$$

•Hence if minimum of $\langle E \rangle$ is E_{min} then $\sum_j \alpha_j (H_{ij} - E_{min} S_{ij}) = 0$.

•This is a set of simultaneous equations for α_j. For a non-trivial solution:

$$|\mathbf{H} - E_{min}\mathbf{S}| = 0$$

•Which can be solved for E_{min} . If system is known to be describable by finite no. of $\psi_j(\mathrm{r})$ this method must give the exact ground state energy.

Rayleigh-Ritz - the hydrogen atom (1)

- This method can be applied to look at the effect of the mass of the nucleus on the ground state wavefunctions of the hydrogen atom.
- We use a linear combination of 1s and 2s orbitals (calculated using an infinitely heavy nucleus), with the true Hamiltonian for the atom.
- The basis functions are:

$$\psi_1 = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-r/a_0}, \qquad \psi_2 = \left(\frac{1}{8\pi a_0^3}\right)^{\frac{1}{2}} (1 - r/2a_0) e^{-r/a_0}$$

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

- The trial function is: $\psi_{trial} = \alpha_1\psi_1 + \alpha_2\psi_2$
- The basis functions are orthonormal so: $S_{11} = S_{22} = 1, \quad S_{12} = S_{21} = 0$
- Where $S_{jk} = \langle \psi_j | \psi_k \rangle$
- The Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}, \qquad \mu = \frac{m_p m_e}{m_p + m_e}$$

Reduced mass

Rayleigh-Ritz -the hydrogen atom (2)

- The matrix elements $H_{jk} = \langle \psi_j | \hat{H} | \psi_k \rangle$ are straightforward to evaluate and given by:

$$H_{11} = \left(\frac{m_e}{m_p} - 1 \right) \frac{\hbar^2}{2a_0^2 m_e}, H_{22} = \frac{1}{4} \left(\frac{m_e}{m_p} - 1 \right) \frac{\hbar^2}{2a_0^2 m_e},$$

$$H_{12} = H_{21} = \frac{16}{27\sqrt{2}} \frac{m_e}{m_p} \frac{\hbar^2}{2a_0^2 m_e}$$

$H_{11}, H_{22} \gg H_{21}, H_{12}$

Note:If we had used the correct wavefunctions for $\hat{H}$ then $H_{12} = H_{21} = 0$

- From above: $|\mathbf{H} - E_{min}\mathbf{S}| = 0$ and $S_{11} = S_{22} = 1, \quad S_{12} = S_{21} = 0$

- So

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

$$= E^2 - (H_{11} + H_{22})E + H_{11}H_{22} - H_{12}H_{21} = 0$$

Rayleigh-Ritz -the hydrogen atom (3)

- Solving this quadratic in E we get:

$$E_{\min} = \frac{1}{8}\frac{\hbar^2}{2a_0^2 m_e}\left(\frac{m_e}{m_p} - 1\right)\left(5 + 3\sqrt{1 + 2\left(\frac{64}{81}\frac{m_e}{m_e - m_p}\right)^2}\right)$$

- Note that if we allow $\frac{m_e}{m_p} \to 0, \quad E = -\frac{\hbar^2}{2a_0^2 m_e}$ as expected.
- With

$$m_e = 9.109 \times 10^{-31} kg, \quad m_p = 1.6726 \times 10^{-27} kg$$

$$E = -\frac{1}{8}\frac{\hbar^2}{2a_0^2 m_e} 0.994559\left(5 + 3\sqrt{\left(1 + 3.71.10^{-7}\right)}\right) \approx -\frac{\hbar^2}{2a_0^2 m_e} 0.994559$$

- This is a reduction in $|E|$ of about 5 parts in 10^3.
- To calculate the wavefunction; we have: $\sum_j \alpha_j (H_{ij} - E_{min} S_{ij}) = 0$.
- So $\alpha_1 \left(H_{11} - E\right) + \alpha_2 H_{12} = 0, \quad \alpha_1 H_{21} + \alpha_2 \left(H_{22} - E\right) = 0$

Rayleigh-Ritz -the hydrogen atom (4)

$$\alpha_1\left(H_{11}-E\right)+\alpha_2 H_{12}=0, \quad \alpha_1 H_{21}+\alpha_2\left(H_{22}-E\right)=0$$

- Which can be solved to give $\dfrac{\alpha_1}{\alpha_2}=-3268$ and since $\alpha_1^2+\alpha_2^2=1$

$$\alpha_1=0.999999953, \alpha_2=-0.000306$$

- The wavefunction is $\psi_{trial}=\alpha_1\psi_1+\alpha_2\psi_2$
- This suggests that the wavefunction now has a very small – 3 parts in 10^4 admixture of the $2s$ wavefunction into the $1s$ wavefunction.
- This result (as well as the decrease in magnitude of the energy) suggests that the electron wavefunction has moved slightly away from the nucleus. The reduced mass used in the Hamiltonian is slightly less than the electron mass and the 'effective particle' has slightly more freedom than an electron.
- Rayleigh-Ritz method has allowed us to calculate the effect of the mass of the nucleus on the ground state energy and wavefunction. For experimental results comparing hydrogen with deuterium see pages 106-7 Haken and Wolf.

Excited States

•If the trial wavefunction is orthogonal to the ground state i.e.

$$c_0 = \int \psi_0^*(\mathrm{r})\phi(\mathrm{r})\,\mathrm{d}^3\mathbf{r} = 0\,,$$

•Then

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_{k=1}^{\infty} E_k\, |c_k|^2}{\sum_{k=1}^{\infty} |c_k|^2} \geq E_1\,.$$

•This is an upper bound for the first excited state. If quantum numbers of ground state are known (e.g angular momentum or parity) ϕ can be chosen to be orthogonal.

•If this is difficult use variational method to approximate ground state and choose ϕ orthogonal to it. This may not work well if ϕ has some admixture of the true ground state.

•When looking for a global minimum be careful not to get stuck at the wrong stationary point!

Lecture 5 - Summary

- Variational method – by varying a trial wavefunction $\phi(\mathrm{r})$ and minimizing the energy we can obtain an upper bound on the energy of the ground state E_0 .

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0 .$$

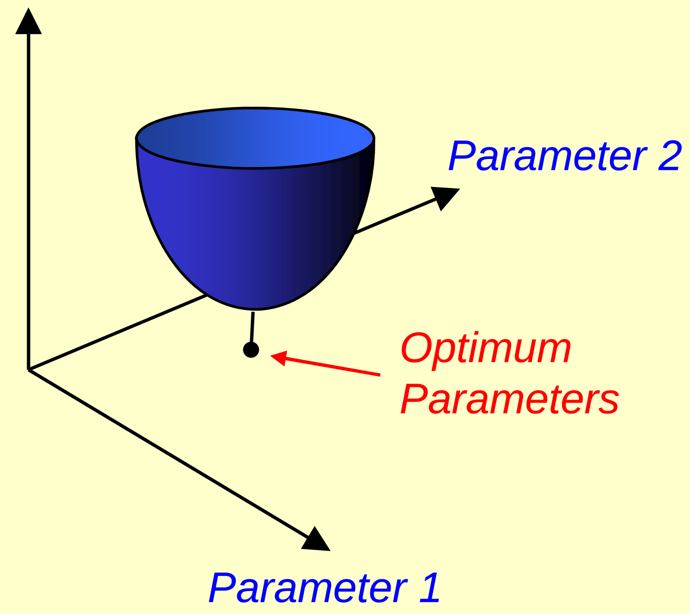
- Example – the ground state energy of the helium atom – calculated using a variable nuclear charge Z' as a free parameter. This gave a result of $Z' = \frac{27}{16}$ and $E_0 \leq -77.4eV$ c/w experimental value: $E_0 = -79.0eV$

- Example – the effect of the mass of the nucleus on the ground state energy and wavefunction of the hydrogen atom. Using a mixture of 1s and 2s wavefunctions as a trial wavefunction $|E|$ was shown to be reduced by 5 parts in 10^3. The 1s wavefunction was modified by the addition of 3 parts in 10^4 of the 2s wavefunction – the effect being that the electron moves slightly away from the nucleus.

- A trial wavefunction orthogonal to the ground state may be used to give an upper bound for the first excited state.

Lecture 5

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$



The End!!

(www.sp.phy.cam.ac.uk/~dar11/pdf)