

I. Variational method

1 Introduction

Useful for the determination of energies and wavefunctions of different atomic states.

H – the time-independent Hamiltonian of the system

E_n – eigenenergies

Ψ_n – eigenfunctions

Schrödinger-equation

$$H\Psi_n = E_n\Psi_n \quad (1)$$

ϕ - wavefunction with finite norm

$E[\phi]$ functional

$$E[\phi] = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}. \quad (2)$$

If $\phi = \Psi_n$ than $E[\phi] \equiv E_n$ eigenstates. We prove, that if

$$\phi = \Psi_n + \delta\phi, \quad (3)$$

than

$$\delta E = 0. \quad (4)$$

We make the variation on (2)

$$\begin{aligned} \delta E[\phi] &= \frac{\int \delta\phi^* H\phi d\tau + \int \phi^* H\delta\phi d\tau}{\int \phi^* \phi d\tau} \\ &\quad - \frac{(\int \delta\phi^* \phi d\tau + \int \phi^* \delta\phi d\tau) \int \phi^* H\phi d\tau}{(\int \phi^* \phi d\tau)^2}, \end{aligned} \quad (5)$$

where we have used $\delta(H\phi) = H\delta\phi$. Using (2) and making $\delta E = 0$ one obtains

$$\int \delta\phi^*(H - E)\phi d\tau + \int \phi^*(H - E)\delta\phi d\tau = 0. \quad (6)$$

Making $\delta\phi \rightarrow i\delta\phi$ we get

$$-i \int \delta\phi^*(H - E)\phi d\tau + i \int \phi^*(H - E)\delta\phi d\tau = 0. \quad (7)$$

Using the above two equations, we can write

$$\int \delta\phi^*(H - E)\phi d\tau = 0 \quad (8)$$

$$\int \phi^*(H - E)\delta\phi d\tau = 0. \quad (9)$$

This should be true for any $\delta\phi$, so the equations are equivalent to the Schrodinger-equation

$$(H - E)\phi = 0. \quad (10)$$

Another important property of the (2) functional is, that gives a superior limit for the ground-state energy E_0 of the system.

We expand ϕ in terms of the Ψ_n eigenfunctions of the Hamiltonian H .

$$\phi = \sum_n a_n \Psi_n. \quad (11)$$

Introducing this expansion to (2)

$$E[\phi] = \frac{\sum_n a_n^* a_n \langle \Psi_n | H | \Psi_n \rangle}{\sum_n a_n^* a_n \langle \Psi_n | \Psi_n \rangle} = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2}, \quad (12)$$

where we have used $H\Psi_n = E_n\Psi_n$. Subtracting the ground-state energy E_0 , we get

$$E[\phi] - E_0 = \frac{\sum_n |a_n|^2 (E_n - E_0)}{\sum_n |a_n|^2}. \quad (13)$$

Using $E_n \geq E_0$, the right side of the equation is nonnegative, so

$$E_0 \leq E[\phi]. \quad (14)$$

In practice we perform the variation only for a class of functions. E.g.: Rayleigh–Ritz method

In this case the trial function $\phi = \phi(\alpha_i, \tau)$ depends on some parameters, so

$$E = E(\alpha_i); \quad \overline{i = 1, n}, \quad (15)$$

If we make the variation on the class of of the trial functions, the $\delta E = 0$ condition is equivalent to

$$\frac{\partial E}{\partial \alpha_i} = 0; \quad \overline{i = 1, n} \quad (16)$$

We can use this method also for the excited states by imposing the orthogonality of ϕ to all states with lower energy

$$\langle \phi | \Psi_n \rangle = 0; \quad \overline{n = 0, i - 1}, \quad (17)$$

2 The Rayleigh–Ritz method for the ground state of the helium

2.1 Simple variational method

We apply the independent electron approximation – product wavefunction

$$\phi(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2), \quad (18)$$

Each $1s$ wavefunction is a hydrogenlike function with 1 parameter – the effective charge α

$$\psi_{1s}(r) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r}. \quad (19)$$

The energy functional:

$$E[\phi] = \langle \phi | H | \phi \rangle. \quad (20)$$

The Hamiltonian:

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (21)$$

where $Z = 2$ is the atomic number

2.1.1 Calculating the matrix element

$$\langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | H | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle$$

Let ψ_i and ψ_j being one-electron normalized wavefunction calculated in a spherical potential. In this case

$$\begin{aligned} \psi_i(\mathbf{r}) &= R_i(r)Y_{l_i m_i}(\theta, \varphi) \\ \psi_j(\mathbf{r}) &= R_j(r)Y_{l_j m_j}(\theta, \varphi), \end{aligned} \quad (22)$$

where $R_i(r)$ and $R_j(r)$ are radial wavefunctions.

The matrix element can be expressed as

$$\begin{aligned} &\langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | H | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle = \\ &= \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | -\frac{\nabla_1^2}{2} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle + \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | -\frac{\nabla_2^2}{2} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle \\ &\quad - \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_1} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle - \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_2} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle \\ &\quad + \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_{12}} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle. \end{aligned} \quad (23)$$

In the first 4 terms the operator acts only on the wavefunction of one electron, so we can separate the integrals for the coordinates of the 2 electrons

$$\begin{aligned} &\langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | H | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle = \\ &= \langle \psi_i(\mathbf{r}_1) | -\frac{\nabla_1^2}{2} | \psi_j(\mathbf{r}_1) \rangle \delta_{i'j'} + \langle \psi'_i(\mathbf{r}_2) | -\frac{\nabla_2^2}{2} | \psi'_j(\mathbf{r}_2) \rangle \delta_{ij} \\ &\quad - \langle \psi_i(\mathbf{r}_1) | \frac{1}{r_1} | \psi_j(\mathbf{r}_1) \rangle \delta_{i'j'} - \langle \psi'_i(\mathbf{r}_2) | \frac{1}{r_2} | \psi'_j(\mathbf{r}_2) \rangle \delta_{ij} \\ &\quad + \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_{12}} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle. \end{aligned} \quad (24)$$

The integrals containing $1/r_k$, $k = 1, 2$ can be easily calculated

$$\begin{aligned}\langle \psi_i(\mathbf{r}_k) | \frac{1}{r_k} | \psi_j(\mathbf{r}_k) \rangle &= \int_0^\infty r_k^2 dr_k R_i^*(r_k) \frac{1}{r_k} R_j(r_k) \int d\hat{\mathbf{r}}_k Y_{l_i m_i}^*(\hat{\mathbf{r}}_k) Y_{l_j m_j}(\hat{\mathbf{r}}_k) \\ &= \int_0^\infty r_k^2 dr_k R_i^*(r_k) \frac{1}{r_k} R_j(r_k) \delta_{l_i l_j} \delta_{m_i m_j}.\end{aligned}\quad (25)$$

In general numerical integration is needed for the calculation of the radial matrix elements.

If the wavefunction is calculated in a $-\alpha/r_k$ Coulomb-potential and $i = j$, than we can calculate analytically

$$\int_0^\infty r_k^2 dr_k R_i^*(r_k) \frac{1}{r_k} R_i(r_k) = \frac{\alpha}{n^2} \quad (26)$$

The matrix elements of the kinetic energy operator $-\nabla_k^2/2$ can be calculated directly, or if ψ_i is eigenfunction of $-\nabla_k^2/2 + V(r_k)$ with eigenvalues E_i then

$$\begin{aligned}\langle \psi_i(\mathbf{r}_k) | -\frac{\nabla_k^2}{2} | \psi_j(\mathbf{r}_k) \rangle &= \\ &= \langle \psi_i(\mathbf{r}_k) | -\frac{\nabla_k^2}{2} + V(r_k) | \psi_j(\mathbf{r}_k) \rangle - \langle \psi_i(\mathbf{r}_k) | V(r_k) | \psi_j(\mathbf{r}_k) \rangle \\ &= \langle \psi_i(\mathbf{r}_k) | E_j | \psi_j(\mathbf{r}_k) \rangle - \langle \psi_i(\mathbf{r}_k) | V(r_k) | \psi_j(\mathbf{r}_k) \rangle \\ &= E_j \delta_{ij} - \langle \psi_i(\mathbf{r}_k) | V(r_k) | \psi_j(\mathbf{r}_k) \rangle.\end{aligned}\quad (27)$$

If the potential is Coulombian $-\alpha/r_k$ then the eigenvalue of the energy is $-\alpha^2/2n^2$, and

$$\langle \psi_i(\mathbf{r}_k) | -\frac{\nabla_k^2}{2} | \psi_j(\mathbf{r}_k) \rangle = -\frac{\alpha^2}{2n_j^2} \delta_{ij} + \alpha \langle \psi_i(\mathbf{r}_k) | \frac{1}{r_k} | \psi_j(\mathbf{r}_k) \rangle. \quad (28)$$

The matrix element of $1/r_{12}$ – we expand the potential in terms of Legendre polynomials

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta), \quad (29)$$

– multipole expansion We express $P_l(\cos \theta)$ in terms of spherical harmonics

$$P_l(\cos \theta) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2). \quad (30)$$

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \sum_{m=-l}^l Y_{lm}^*(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2). \quad (31)$$

Further

$$\begin{aligned}
& \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_{12}} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle = \\
& = \sum_l \frac{4\pi}{2l+1} \int_0^\infty dr_1 r_1^2 R_i^*(r_1) R_j(r_1) \int_0^\infty dr_2 r_2^2 R_i^*(r_2) \frac{r_2^l}{r_2^{l+1}} R'_j(r_2) \\
& \quad \times \sum_m \int Y_{l_i m_i}^*(\hat{\mathbf{r}}_1) Y_{l_m}^*(\hat{\mathbf{r}}_1) Y_{l_j m_j}(\hat{\mathbf{r}}_1) d\hat{\mathbf{r}}_1 \\
& \quad \times \int Y_{l'_i m'_i}^*(\hat{\mathbf{r}}_2) Y_{l_m}(\hat{\mathbf{r}}_2) Y_{l'_j m'_j}(\hat{\mathbf{r}}_2) d\hat{\mathbf{r}}_2. \tag{32}
\end{aligned}$$

The integral of the product of 3 spherical harmonics is

$$\int Y_{l_a m_a}^*(\hat{\mathbf{r}}) Y_{l_b m_b}(\hat{\mathbf{r}}) Y_{l_c m_c}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \sqrt{\frac{(2l_b+1)(2l_c+1)}{4\pi(2l_a+1)}} C_{l_b 0 l_c 0}^{l_a 0} C_{l_b m_b l_c m_c}^{l_a m_a}, \tag{33}$$

– C – Clebsch–Gordan coefficient In order to have nonzero terms \mathbf{l}_a should be the vectorial sum of \mathbf{l}_b and \mathbf{l}_c , meaning that

$$m_a = m_b + m_c, \tag{34}$$

and

$$|l_a - l_c| \leq l_b \leq l_a + l_c \tag{35}$$

$C_{l_b 0 l_c 0}^{l_a 0}$ is nonzero only for even $l_a + l_b + l_c$

The matrix element of $1/r_{12}$ will be nonzero if

$$m_j - m_i = m'_i - m'_j \tag{36}$$

$$|l'_i - l'_j| \leq l_i + l_j \tag{37}$$

$$|l_i - l_j| \leq l'_i + l'_j \tag{38}$$

$$l_i + l_j + l'_i + l'_j \quad \text{even} \tag{39}$$

In these cases we obtain

$$\begin{aligned}
& \langle \psi_i(\mathbf{r}_1)\psi'_i(\mathbf{r}_2) | \frac{1}{r_{12}} | \psi_j(\mathbf{r}_1)\psi'_j(\mathbf{r}_2) \rangle = \\
& = \sum_{l=\max\{|l_i-l_j|, |l'_i-l'_j|\}}^{\min\{l_i+l_j, l'_i+l'_j\}} \int_0^\infty dr_1 r_1^2 R_i^*(r_1) R_j(r_1) \int_0^\infty dr_2 r_2^2 R_i^*(r_2) \frac{r_2^l}{r_2^{l+1}} R'_j(r_2) \\
& \times \sqrt{\frac{(2l_i+1)(2l'_j+1)}{(2l_j+1)(2l'_i+1)}} C_{l 0 l_i 0}^{l_j 0} C_{l 0 l'_j 0}^{l'_i 0} \sum_{m_i m_j m'_i m'_j} C_{l, m_j - m_i, l_i m_i}^{l_j m_j} C_{l m_j - m_i, l'_j m'_j}^{l'_i m'_i}. \tag{40}
\end{aligned}$$