Variational methods

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Ritz variational principle

For Hamiltonians bounded from below (there exists a smallest eigenvalue)

$$\frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} > \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\,, \qquad \text{ahol} \quad H|\psi\rangle = E|\psi\rangle$$

Let $|\varphi\rangle$ depend on some α parameter and let α_0 be the solution of

$$E(\alpha) = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle}, \qquad \frac{dE}{d\alpha} = 0.$$

Then $E(\alpha_0)$ and $|\varphi(\alpha_0)\rangle$ is an approximation of the ground state energy and wave-function.

Harmonic oscillator

Hamiltonian of the harmonic oscillator with frequency ω

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{1}{2}m\omega^2 x^2$$

Let us use the follwoing trial wave-function $\varphi(x) = e^{-\alpha x^2}$
The norm of which is the following:

$$\langle\varphi|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x e^{-2\alpha x^2} = \sqrt{\frac{\pi}{2\alpha}}$$

Harmonic oscillator

Effect of the Hamiltonian on the trial wave-function:

1. First the second derivative term

$$\frac{\mathrm{d}}{\mathrm{d}x}e^{-\alpha x^2} = -2\alpha x e^{-\alpha x^2}, \quad \frac{\mathrm{d}^2}{\mathrm{d}x^2}e^{-\alpha x^2} = \left(-2\alpha + 4\alpha x^2\right) e^{-\alpha x^2}$$

2. Now the energy integral:

$$\langle\varphi|H|\varphi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x \left(-\frac{\hbar^2}{2m}\left(-2\alpha + 4\alpha x^2\right) + \frac{1}{2}m\omega^2 x^2\right) e^{-2\alpha x^2}$$

$$= \frac{\hbar^2}{m}\alpha \int_{-\infty}^{\infty} \mathrm{d}x e^{-2\alpha x^2} + \left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right) \int_{-\infty}^{\infty} dx x^2 e^{-2\alpha x^2}$$

Harmonic oscillator

Now the second integral is performed as

$$\int_{-\infty}^{\infty} \mathrm{d}x x^2 e^{-2\alpha x^2} = -\frac{1}{4\alpha} x e^{-2\alpha x^2}\Big|_{-\infty}^{\infty} + \frac{1}{4\alpha}\int_{-\infty}^{\infty} \mathrm{d}x e^{-2\alpha x^2}$$

Where only the second term survives, tigether with the normalization yielding a contribution of $\frac{1}{4\alpha}$

$$E(\alpha) = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \frac{\hbar^2}{m}\alpha + \left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right)\frac{1}{4\alpha}$$

$$= \frac{\hbar^2}{2m}\alpha + \frac{1}{8}m\omega^2\frac{1}{\alpha}$$

Harmonic oscillator

Now find the optimal α that minimizes the energy integral,

$$\frac{\mathrm{d}E(\alpha)}{\mathrm{d}\alpha} = 0 \rightarrow \frac{\hbar^2}{2m} - \frac{1}{8}m\omega^2\frac{1}{\alpha^2} = 0 \rightarrow \alpha_0 = \frac{m\omega}{2\hbar}, \quad E = \frac{1}{2}\hbar\omega$$

Note that we just recovered the exact ground state function and energy, this because we started from the form of the known wave-function.

H atom

Hamiltonian of the H atom

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{ke^2}{r}$$

By introducing the $a_0 = \frac{\hbar^2}{ke^2 m}$, $E_0 = \frac{ke^2}{a_0}$ atomic units

$$H = -\frac{1}{2}\Delta - \frac{1}{r}\,.$$

Distance is measured in Bohr units ($a_0 = 0.529\,\mathring{A}$) while energy in Hartree units ($1\ H = 27.2\,eV$).

H atom

We are looking for the ground state energy. Let the trial function be of the form $e^{-\alpha r}$, $l = 0$.

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

Norm of the trial function:

$$\langle\varphi|\varphi\rangle = \int_0^\infty e^{-2\alpha}r^2 dr = \frac{2}{(2\alpha)^3} = \frac{1}{4\alpha^3}$$

Effect of the Hamiltonian on the trial wave-function:

$$\begin{aligned} H|\varphi\rangle &= -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}e^{-\alpha r} - \frac{1}{r}e^{-\alpha r} = \frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\alpha e^{-\alpha r} - \frac{1}{r}e^{-\alpha r} \\ &= \frac{1}{2}\frac{1}{r^2}\left(2r\alpha - r^2\alpha^2\right)e^{-\alpha r} - \frac{1}{r}e^{-\alpha r} \end{aligned}$$

H atom

Expectation value of the Hamiltonian:

$$\langle\varphi|H|\varphi\rangle = \int_0^\infty \frac{1}{2}\frac{1}{r^2}\left(2r\alpha - r^2\alpha^2\right)e^{-2\alpha r}r^2dr - \int_0^\infty -\frac{1}{r}e^{-2\alpha r}r^2dr = \frac{1}{8\alpha} - \frac{1}{4\alpha^2}$$

$$E(\alpha) = \frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \left(\frac{1}{8\alpha} - \frac{1}{4\alpha^2}\right)4\alpha^3 = \frac{1}{2}\alpha^2 - \alpha$$

In the case of lowest possible value the derivative with respect to the parameter the epectation value vanishes:

$$\frac{\partial E}{\partial \alpha} = \alpha - 1 = 0\,, \quad \alpha = 1$$

If we choose this optimal value of α, the energy of the H atom will be exactly $E = -\frac{1}{2}$ in atomic units, i.e. Hartree units. The equivalene with the *exact value* is the consequence of the fact that the trial function was exactly of the same form as the *real* ground state wave-function.

He atom $S = 0$ ground state

We can look for the wave-function of the He atom in a form of the product of the H atomic wave-functions:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(r_1)\varphi(r_2)\frac{1}{\sqrt{2}}\left(|1/2, 1/2\rangle|1/2, -1/2\rangle - |1/2, -1/2\rangle|1/2, 1/2\rangle\right)$$

$$= \underbrace{\begin{vmatrix} \varphi(r_1)|1/2, 1/2\rangle & \varphi(r_1)|1/2, -1/2\rangle \\ \varphi(r_2)|1/2, 1/2\rangle & \varphi(r_2)|1/2, -1/2\rangle \end{vmatrix}}_{\text{Slater determináns}}$$

Hamiltonian of the He atom:

$$H = -\frac{1}{2}\Delta_1 - \frac{2}{r_1} - \frac{1}{2}\Delta_2 - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = H(1) + H(2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\langle\Phi|H|\Phi\rangle = \langle\varphi(1)|H(1)|\varphi(1)\rangle + \langle\varphi(2)|H(2)|\varphi(2)\rangle + \langle\varphi(r_1)\varphi(r_2)|\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}|\varphi(r_1)\varphi(r_2)\rangle$$

$$\langle\Phi|\Phi\rangle = \langle\varphi|\varphi\rangle\langle\varphi|\varphi\rangle$$

He atom $S = 0$ ground state

Let the trial wave-function be of the form $\varphi(r) = 4\alpha^3 e^{-\alpha r}$, similarly to the case of the H atom:

$$\langle\varphi|\varphi\rangle = 1, \qquad \langle\varphi|H|\varphi\rangle = \frac{1}{2}\alpha^2 - 2\alpha$$

However the integral $\langle\varphi(r_1)\varphi(r_2)|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}|\varphi(r_1)\varphi(r_2)\rangle$ is far from trivial to compute:

- Multipole expansion:
$$\frac{1}{|r-r'|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^m(\vartheta,\varphi) Y_l^m(\vartheta',\varphi')$$
- Bring it to the form of a Poisson equation:

Let's choose another strategy!

He atom $S = 0$ ground state

$$\langle\varphi(r_1)\varphi(r_2)|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}|\varphi(r_1)\varphi(r_2)\rangle = \int d\mathbf{r}_1^3\varphi^*(r_1)\underbrace{\int d\mathbf{r}_2^3\frac{|\varphi(r_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}}_{\substack{\text{electric potential}\\ \text{of}\\ \text{a}\\ \text{charge}\\ \text{density}}}\varphi(r_1)$$

Hartree potential:

$$V_H(\mathbf{r}_1) = \int d\mathbf{r}_2^3\frac{|\varphi(r_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}, \qquad \Delta V_H = -|\varphi|^2 \qquad \text{(Poisson equation)}$$

$$\Delta V_H = -4\alpha^3 e^{-2\alpha r}$$

Poisson equation in spherical coordinates:

$$\frac{1}{r}\frac{\partial^2 r V_H}{\partial r^2} = -4\alpha^3 e^{-2\alpha r}\ .$$

Partial derivatives can substituted by total derivatives

He atom $S = 0$ ground state

WE can easily solve the differential equation by two successive integration:

$$\frac{dU}{dr} = -4\alpha^3 \int r e^{-2\alpha r} dr = \alpha(2\alpha r + 1)e^{-2\alpha r} + C$$

$$U = \int \alpha(2\alpha r + 1)e^{-2\alpha r} dr + Cr = -(r\alpha + 1)e^{-2\alpha r} + Cr + B$$

Nevertheless, we are left with two free parameters, fixed by boundary conditions. At infinite distance one should feel a point charge implying a decay of the potential $\sim 1/r$, i.e.: $\lim_{r\to\infty} U(r) = 1$, while we can always choose the origo as the zero-point of the potential : $C = 0$ és $B = 1$.

$$V_H = \frac{1}{r} - \frac{1 + \alpha r}{r} e^{-2\alpha r}$$

Now we can calculate the matrix element of the Hartrre potential:

$$E_C = \langle\varphi|V_H|\varphi\rangle = 4\alpha^3 \int_0^\infty (\frac{1}{r} - \frac{1 + \alpha r}{r} e^{-2\alpha r}) e^{-2\alpha r} r^2 dr = \frac{5}{8}\alpha$$

He atom $S = 0$ ground state

$$E(\alpha) = \alpha^2 - 4\alpha + \frac{5}{8}\alpha \ , \quad \frac{dE}{d\alpha} = 2\alpha - \frac{27}{8} \ . \tag{1}$$

The optimal α parameter $\alpha = \frac{27}{16}$ and the corresponding energy $E = -\left(\frac{27}{16}\right)^2 = -2.847$. The exact ground state energy is -2.903 Hartree, being smaller only by some hundredth Hartree as the one given by the variational method with independent H atomic wave-function, but keep in mind, that 0.056 Hartree measured in electron-volts is $\Delta E = 1.52eV$

Homework

Consider the Hamiltonian of the so called Moshinsky atom describing 2 spin one-half particles:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}m\Omega^2(x_1^2 + x_2^2) + \frac{1}{2}m\omega^2(x_1 - x_2)^2 \ .$$

- Introduce the variables $X = x_1 + x_2$ and $x = x_1 - x_2$ and solve the time-independent Schrödinger-equation. What are the symmetries of the spatial parts of the $S = 0$ singlet and $S = 1$ triplet solutions?
- Using the variational method derive the equation for the $S = 0$ ground state wave-function and solve it (Hartree-Fock equation)! Hint: Variate/differentiate with respect to φ^* the expression $\langle\varphi(x_1)\varphi(x_2)|H|\varphi(x_1)\varphi(x_2)\rangle)$ taking into account, with the usual Lagrange multiplicator method, the costraint $\langle\varphi|\varphi\rangle = 1$