Description of the method

We describe the solution of the Schrödinger equation using Ritz method and Hermite functions basis.

Description

We want to solve the variational equation

$$\delta\Pi[\psi] = 0\, ,$$

with

$$\Pi[\psi] = \frac{1}{2}\langle\nabla\psi, \nabla\psi\rangle + \langle\psi, V(x)\psi\rangle - E\langle\psi, \psi\rangle\, ,$$

being ψ the wave function, $V(x)$ the potential and E the energy. This variational formulation is equivalent to the time-independent Schrödinger equation, and E works as a Lagrange multiplier to enforce that the probability over the whole domain is 1.

We can expand the wave function in an orthonormal basis, namely

$$\psi = \sum_{n=0}^{N} c_n u_n(x)\, ,$$

where $u_n(x) \equiv \mu_n H_n(x) e^{-x^2/2}$ is a normalized Hermite function, μ_n is the inverse of magnitude of the nth Hermite polynomial

$$\mu_n = \frac{1}{\sqrt{\pi^{1/2} n! 2^n}}\, ,$$

and c_n are the coefficients of the expansion. This representation is exact in the limit $N \to \infty$.

If we replace the expansion in the functiona, we obtain

$$\Pi_N = \sum_{m=0}^{N}\sum_{n=0}^{N} c_m c_n \left[\frac{1}{2}\langle \nabla u_m, \nabla u_n\rangle + \langle u_m, V(x) u_n\rangle - E^N \delta_{mn}\right] .$$

The integral involving the two derivatives reads

$$\begin{aligned} u'_m u'_n = &\left[2m\frac{\mu_{m-1}}{\mu_m} u_{m-1} - x u_m\right]\left[2n\frac{\mu_{n-1}}{\mu_n} u_{n-1} - x u_n\right] \\ =&4mn\frac{\mu_{m-1}\mu_{n-1}}{\mu_m \mu_n} u_{n-1}u_{m-1} - 2m\frac{\mu_{m-1}}{\mu_m} x u_{m-1} u_n \\ &- 2n\frac{\mu_{n-1}}{\mu_n} x u_{n-1} u_m + x^2 u_m u_n \end{aligned}$$

Thus, the kinetic energy term reads

$$\begin{aligned} \langle \nabla u_m, \nabla u_n\rangle =&4mn\frac{\mu_{m-1}\mu_{n-1}}{\mu_m \mu_n}\langle u_{n-1}, u_{m-1}\rangle - 2m\frac{\mu_{m-1}}{\mu_m}\langle u_{m-1}, x u_n\rangle \\ &- 2n\frac{\mu_{n-1}}{\mu_n}\langle u_m, x u_{n-1}\rangle + \langle u_m, x^2 u_n\rangle \\ =&4mn\frac{\mu_{m-1}^2}{\mu_m^2}\delta_{mn} - 2m\frac{\mu_{m-1}}{\mu_m}\alpha_{m-1,n} - 2n\frac{\mu_{n-1}}{\mu_n}\alpha_{m,n-1} + \beta_{mn} , \end{aligned}$$

with

$$\alpha_{m,n} \equiv \langle u_m, x u_n\rangle = \begin{cases} \sqrt{\frac{n+1}{2}} & m = n+1 \\ \sqrt{\frac{n}{2}} & m = n-1 \\ 0 & \text{otherwise} \end{cases} ,$$

and

$$\beta_{m,n} \equiv \langle u_m, x^2 u_n\rangle = \begin{cases} \frac{\sqrt{n(n-1)}}{2} & m = n-2 \\ \frac{2n+1}{2} & m = n \\ \frac{\sqrt{(n+1)(n+1)}}{2} & m = n+2 \\ 0 & \text{otherwise} \end{cases} .$$

The functional is rewritten as

$$
\begin{aligned}
\Pi_N = \sum_{m=0}^{N}\sum_{n=0}^{N} c_m c_n \Bigg[& 2mn\frac{\mu_{m-1}^2}{\mu_m^2}\delta_{mn} - m\frac{\mu_{m-1}}{\mu_m}\alpha_{m-1,n} - n\frac{\mu_{n-1}}{\mu_n}\delta_{m,n-1} \\
& -\frac{1}{2}\beta_{mn} + \langle u_m, V(x)u_n\rangle - E^N\delta_{mn}\Bigg] \,. \qquad (1)
\end{aligned}
$$

Taking the variation

$$
\delta\Pi_N = 0 \,,
$$

that in this case is equivalent to

$$
\frac{\partial \Pi_N}{\partial c_i} = 0 \quad \forall i = 0, 1, \cdots N \,,
$$

yields to

$$
[H]\{c\} = E^N\{c\} \,,
$$

with

$$
H_{mn} = 2mn\frac{\mu_{m-1}^2}{\mu_m^2}\delta_{mn} - m\frac{\mu_{m-1}}{\mu_m}\alpha_{m-1,n} - n\frac{\mu_{n-1}}{\mu_n}\delta_{m,n-1} - \frac{1}{2}\beta_{mn} + \langle u_m, V(x)u_n\rangle \,.
$$

The last integral is computed using Gauss-Hermite quadrature.