KVANTNA MEHANIKA

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17 Varijacijski princip

17.1 Nađite aproksimativnu vrijednost energije osnovnog stanja jednodimenzionalnog harmoničkog oscilatora pomoću varijacijskog principa. Za probnu funkciju uzmite

$$\psi(x) = A\mathrm{e}^{-bx^2}$$

17.2 Nađite aproksimativnu vrijednost energije vezanog stanja (pa prema tome i osnovnog stanja) za česticu u potencijalu oblika delta funkcije $V = -\alpha\delta(x)$ koristeći varijacijski princip. Za probnu funkciju uzmite

$$\psi(x) = A\mathrm{e}^{-bx^2}$$

Prisjetimo se: točna energija vezanog stanja glasi

$$E_g = -\frac{m\alpha^2}{2\hbar^2}$$

17.3 Nađite aproksimativnu vrijednost energije osnovnog stanja za česticu u jednodimenzionalnoj, beskonačnoj, pravokutnoj jami širine a. Za probnu funkciju uzmite

$$\psi(x) = \begin{cases} Ax\,, & 0 \le x \le a/2 \\ A(a-x)\,, & a/2 \le x \le a \\ 0\,, & \text{drugo} \end{cases}$$

17.4 ***Feynman-Hellmannov teorem*** Promotrite valnu funkciju $\psi(\alpha_1, \alpha_2, ..., \alpha_n; \mathbf{r})$ u kojoj su $\alpha_1, \alpha_2, ..., \alpha_n$ parametri. Neka je ψ normalizirana i neka su parametri takvi da je

$$E(\alpha_1, \alpha_1, ..., \alpha_n) = \int \psi^* H \psi \, \mathrm{d}^3 r$$

minimum, gdje je H hamiltonijan sustava.

(a) Pokažite da parametre možemo odrediti iz sustava jednadžbi

$$\int \psi^* H \frac{\partial \psi}{\partial \alpha_i} \mathrm{d}^3 r - \mu \int \psi^* \frac{\partial \psi}{\partial \alpha_i} \mathrm{d}^3 r = 0 \quad \text{za } i = 1, 2, ..., n$$

gdje je μ Lagrangeov multiplikator.

(b) Pretpostavimo da hamiltonijan H ovisi o parametru λ (na primjer, nuklearni naboj ili udaljenost između atomskih jezgri u molekuli). Tada će i parametri α_i ovisiti o λ. Dokažite jednakost

$$\frac{\mathrm{d}E}{\mathrm{d}\lambda} = \int \psi^* \frac{\partial H}{\partial \lambda} \psi \, \mathrm{d}^3 r$$

poznatu pod imenom Feynman-Hellmannov teorem.

(c) Upotrijebite gornji teorem da nađete $\langle V \rangle$ kod jednodimenzionalnog harmoničkog oscilatora. Uzmite $\lambda = \omega$. Slično, uzmite $\lambda = \hbar$ te izračunajte $\langle T \rangle$.

17.5 ***Linearna kombinacija atomskih orbitala (LCAO)*** Nađite aproksimativnu vrijednost energije osnovnog stanja za ioniziranu molekulu vodika H_2^+. Koristite varijacijski princip i probnu funkciju oblika

$$\psi(x) = \frac{1}{\sqrt{\pi a_0^3}} \mathrm{e}^{-r/a_0}$$

te pretpostavite da se protoni nalaze na fiksnoj udaljenosti R. Varijabla R postat će varijacijski parametar.

17.6 Neka je za zadani hamiltonijan poznato prvih $n - 1$ svojstvenih stanja obzirom na rastuću energiju svakog od stanja. Napišite izraz kojim se pomoću varijacijskog principa dobiva gornja granica za svojstvenu vrijednost hamiltonijana za n-ti energetski nivo.
Uputa: računajte najprije za $n = 2$. Formirajte stanje $|\, g\rangle = |\, f\,\rangle - |\psi_1\rangle\langle\psi_1|\, f\,\rangle$ gdje je $|\psi_1\rangle$ prvo svojstveno stanje hamiltonijana H koje je normalizirano (vrijedi $\langle\psi_1|\psi_1\rangle = 1$), a $|\, f\,\rangle$ stanje koje odgovara probnoj funkciji $f(\mathbf{r})$. Normalizirajte $|\, g\rangle$ i provjerite da je $\langle\psi_1|\, g\rangle = 0$. Pomoću uvjeta normalizacije pokažite da je varijacijski izraz $\langle g|\, H\,|\, g\rangle \geq E_2$.

17.1

Normalizacija probne funkcije $\psi = A e^{-bx^2}$

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

$$|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} = 1$$

$$\Rightarrow \quad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

Hamiltonijan za jednodimenzionalni harmonički oscilator

$$H = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{T} + \underbrace{\frac{1}{2} m\omega^2 x^2}_{V}$$

$$E(b) = \langle H \rangle = \langle T \rangle + \langle V \rangle$$

$$\langle T \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx$$

$$\frac{d^2}{dx^2}\left(e^{-bx^2}\right) = \frac{d}{dx}\left[e^{-bx^2}\cdot(-2bx)\right] = (-2b)\left[e^{-bx^2} + x e^{-bx^2}\cdot(-2bx)\right]$$

$$\langle T \rangle = \frac{\hbar^2 |A|^2}{2m}(2b)\left\{(-2b)\int_{-\infty}^{\infty} e^{-2bx^2}\cdot x^2 dx + \int_{-\infty}^{\infty} e^{-2bx^2} dx\right\}$$

$$\int_{-\infty}^{\infty} e^{-2bx^2} dx = \sqrt{\frac{\pi}{2b}}$$

$$\int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{1}{4b}\sqrt{\frac{\pi}{2b}}$$

$$\langle T \rangle = \frac{\hbar^2}{2m}(2b)\cdot\sqrt{\frac{2b}{\pi}}\left\{\underbrace{(-2b)\cdot\frac{1}{4}\sqrt{\frac{\pi}{2b}}}_{1/2} + \sqrt{\frac{\pi}{2b}}\right\}$$

$$= \frac{\hbar^2}{2m} b$$

$$\langle V \rangle = \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\cdot x^2 dx = \frac{1}{2} m\omega^2 \sqrt{\frac{2b}{\pi}}\cdot\frac{1}{4b}\sqrt{\frac{\pi}{2b}}$$

$$= \frac{m\omega^2}{8b}$$

$$E(b) = \frac{\hbar^2}{2m} b + \frac{m\omega^2}{8}\cdot\frac{1}{b}$$

$$\frac{dE}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8}\cdot\frac{1}{b^2} = 0 \Rightarrow \quad b_0 = \frac{m\omega}{2\hbar}$$

$$E(b_0) = \frac{\hbar^2}{2m} \cdot \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \cdot \frac{2\hbar}{m\omega} = \frac{\hbar\omega}{2}$$

To je upravo TOČNA energija osnovnog stanja za harmonički oscilator.
Točna vrijednost je posljedica dobrog odabira probne funkcije.

$\boxed{17.2}$

Normalizacija probne funkcije daje $A = \left(\frac{2b}{\pi}\right)^{1/4}$ iz prošlog zadatka. Hamiltonijan glasi

$$H = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{T} \underbrace{- \alpha\delta(x)}_{V}$$

$$\langle T \rangle = \frac{\hbar^2}{2m} b$$

$$\langle V \rangle = -\alpha |A|^2 \int_{-\infty}^{\infty} \underbrace{e^{-2bx^2}\delta(x)}_{1} dx = -\alpha\sqrt{\frac{2b}{\pi}}$$

$$E(b) = \langle H \rangle = \langle T \rangle + \langle V \rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}.$$

$$\frac{dE}{db} = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \Rightarrow b_0 = \frac{2m^2\alpha^2}{\pi\hbar^4}$$

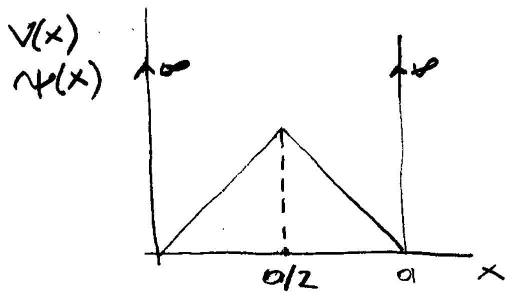
$$E(b_0) = \frac{\hbar^2}{2m}\cdot\frac{2m^2\alpha^2}{\pi\hbar^4} - \alpha\cdot\sqrt{\frac{2}{\pi}\cdot\frac{2m^2\alpha^2}{\pi\hbar^4}}.$$

$$= \frac{m\alpha^2}{\pi\hbar^2} - \alpha\cdot\frac{2m\alpha^2}{\pi\hbar^2} = -\frac{m\alpha^2}{\pi\hbar^2}$$

Vidimo da je

$$-\frac{m\alpha^2}{2\hbar^2} < -\frac{m\alpha^2}{\pi\hbar^2}$$

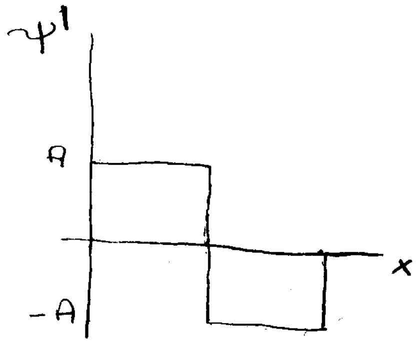
17.3



$$\psi(x) = \begin{cases} Ax; & 0 \le x \le a/2 \\ A(a-x); & a/2 \le x \le a \\ 0; & \text{drugo} \end{cases}$$

Prva derivacija (ne postoji u točkama: 0, a/2, a)

$$\frac{d\psi}{dx} = \begin{cases} A; & 0 \le x \le a/2 \\ -A; & a/2 \le x \le a \\ 0; & \text{drugo} \end{cases} \qquad \frac{d\psi}{dx} = A\,\Theta(x) - 2A\,\Theta\left(x - \frac{a}{2}\right) + A\,\Theta(x-a)$$



Graf za 1. derivaciju

Druga derivacija (derivacija step-funkcije)

$$\frac{d^2\psi}{dx^2} = A\,\delta(x) - 2A\,\delta\left(x - \frac{a}{2}\right) + A\,\delta(x-a)$$

Normalizacija

$$1 = \int_0^a |\psi|^2 dx = |A|^2 \left\{ \int_0^{a/2} x^2 dx + \int_{a/2}^{a} (a-x)^2 dx \right\}$$

$$= |A|^2 \left\{ \frac{1}{3} \cdot \frac{a^3}{8} + \frac{1}{3} \frac{a^3}{8} \right\} = |A|^2 \cdot \frac{a^3}{12}$$

$$\Rightarrow A = \frac{2\sqrt{3}}{a\sqrt{a}}$$

Hamiltonijan

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$E = \langle H \rangle = -\frac{\hbar^2}{2m} \int_0^a \psi \underbrace{\frac{d^2\psi}{dx^2}}_{= \left[A\,\delta(x) - 2A\,\delta\left(x - \frac{a}{2}\right) + A\,\delta(x-a)\right]} dx =$$

$$E = -\frac{\hbar^2 A}{2m}\left\{ \psi(0) - 2\psi\left(\frac{a}{2}\right) + \psi(a) \right\} = -\frac{\hbar^2 A}{2m} \cdot \left(-2A\frac{a}{2}\right) = \frac{12\hbar^2}{2ma^2}$$

pogledati kako izgleda ψ na crtežu

Prava energija: $E_g = \frac{\pi^2 \hbar^2}{2ma^2}$

Vidimo: $E_g \leq E$

17.4

(a) Tražimo ekstrem funkcije

$$E(\alpha_1, \alpha_2, \dots, \alpha_n) = \int \psi^* H \psi \, d^3r$$

uz uvjet

$$\int \psi^* \psi \, d^3r = 1$$

Potražimo varijaciju

$$\delta E = \int \delta\psi^* H \psi \, d^3r + \int \psi^* H \delta\psi \, d^3r \qquad (*)$$

$$\int \delta\psi^* \psi \, d^3r + \int \psi^* \delta\psi \, d^3r = 0 \qquad (**)$$

ψ i ψ^* su funkcije od parametara $\{\alpha_i, i=1, \dots, n\}$ i $\{\alpha_i^*, i=1, \dots, n\}$

$$\delta\psi = \sum_{i=1}^{n} \frac{\partial\psi}{\partial\alpha_i} \delta\alpha_i$$

$$\delta\psi^* = \sum_{i=1}^{n} \frac{\partial\psi^*}{\partial\alpha_i^*} \delta\alpha_i^*$$

Uvrstimo u $(*)$ i $(**)$

$$\delta E = \sum_{i=1}^{n} \delta\alpha_i^* \int \frac{\partial\psi^*}{\partial\alpha_i^*} H \psi \, d^3r + \sum_{i=1}^{n} \delta\alpha_i \int \psi^* H \frac{\partial\psi}{\partial\alpha_i} d^3r$$

$$\sum_{i=1}^{n} \left\{ \delta\alpha_i^* \int \frac{\partial\psi^*}{\partial\alpha_i^*} \psi \, d^3r + \delta\alpha_i \int \psi^* \frac{\partial\psi}{\partial\alpha_i} d^3r \right\} = 0$$

Pomnožimo drugu jednadžbu sa μ i oduzmemo od prve i izjednačimo s 0

$$\delta E = \sum_{i=1}^{n} \left\{ \delta\alpha_i^* \int \frac{\partial\psi^*}{\partial\alpha_i^*} (H-\mu) \psi \, d^3r + \delta\alpha_i \int \psi^* (H-\mu) \frac{\partial\psi}{\partial\alpha_i} d^3r \right\} = 0$$

Varijacije parametara $\delta\alpha_1, \dots, \delta\alpha_n, \delta\alpha_1^*, \dots, \delta\alpha_n^*$ su linearno zavisne. No, imamo parametar μ i njega postavljamo tako da je npr.

$$\int \frac{\partial\psi^*}{\partial\alpha_1^*} (H-\mu) \psi \, d^3r = 0$$

Time smo eliminirali linearnu zavisnost varijacija, te su ostale varijacije linearno nezavisne. Možemo pisati:

$$\int \frac{\partial \psi^*}{\partial \alpha_i^*}(H-\mu)\psi \, d^3r = 0 \quad \text{za} \quad i = 2,3,\dots,n$$

i

$$\int \psi^*(H-\mu)\frac{\partial \psi}{\partial \alpha_i} d^3r = 0 \quad \text{za} \quad i = 1,2,\dots,n$$

Budući je $\delta E = 0$, E ima ekstrem za vrijednosti parametara

$$\alpha_1 = \alpha_{10}$$
$$\alpha_2 = \alpha_{20}$$
$$\vdots$$
$$\alpha_n = \alpha_{n0}$$

(b)

$$E(\alpha_1,\dots,\alpha_n) = \int \psi^* H \psi \, d^3r$$

$$\frac{dE}{d\lambda} = \int \frac{\partial \psi^*}{\partial \lambda} H \psi \, d^3r + \int \psi^* \frac{\partial H}{\partial \lambda} \psi \, d^3r + \int \psi^* H \frac{\partial \psi}{\partial \lambda} d^3r$$

$$\frac{\partial \psi}{\partial \lambda} = \sum_{i=1}^{n} \frac{\partial \psi}{\partial \alpha_i} \cdot \frac{\partial \alpha_i}{\partial \lambda}$$

$$\frac{\partial \psi^*}{\partial \lambda} = \sum_{i=1}^{n} \frac{\partial \psi^*}{\partial \alpha_i^*} \frac{\partial \alpha_i^*}{\partial \lambda}$$

Uvjet normalizacije

$$\frac{d}{d\lambda} \int \psi^* \psi \, d^3r = 0$$

$$\int \frac{\partial \psi^*}{\partial \lambda} \psi \, d^3r + \int \psi^* \frac{\partial \psi}{\partial \lambda} d^3r = 0$$

Imamo

$$\frac{dE}{d\lambda} = \sum_{i=1}^{n} \frac{\partial \alpha_i^*}{\partial \lambda}\left[\int \frac{\partial \psi^*}{\partial \alpha_i^*}(H-\mu)\psi \, d^3r\right] + \frac{\partial \alpha_i}{\partial \lambda}\left[\int \psi^*(H-\mu)\frac{\partial \psi}{\partial \alpha_i} d^3r\right]\Big\}$$
$$+ \int \psi^* \frac{\partial H}{\partial \lambda} \psi \, d^3r$$

Ako je $\delta E = 0$ odnosno $E(\alpha_{10},\dots,\alpha_{n0}) = E$ energije tada su izrazi

$$[\quad] = 0 \quad \text{zbog (a)}$$

$$\Rightarrow \frac{dE}{d\lambda} = \int \psi^* \frac{\partial H}{\partial \lambda} \psi \, d^3r$$

(c) Harmonički oscilator

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2 x^2}{2}$$

$$E = \langle H \rangle = \hbar\omega\left(n+\frac{1}{2}\right)$$

$$\frac{dE}{d\omega} = \hbar\left(n+\frac{1}{2}\right)$$

$$\langle H \rangle = \int \psi^* \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2 x^2}{2}\right)\psi \, dx$$

Feynman-Hellmann

$$\frac{dE}{d\omega} = \int \psi^* \cdot m\omega x^2 \cdot \psi \, dx = \frac{2}{\omega}\int \psi^* \underbrace{\frac{m\omega^2}{2} x^2}_{V(x)} \psi \, dx$$

Izjednačimo

$$\frac{2}{\omega}\langle V \rangle = \hbar\left(n+\frac{1}{2}\right)$$

$$\Rightarrow \langle V \rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right)$$

Slično

$$\frac{dE}{d\hbar} = \omega\left(n+\frac{1}{2}\right)$$

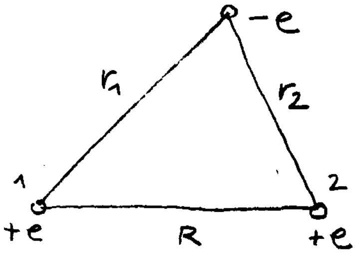
$$\frac{dE}{d\hbar} = \int \psi^* \left(-\frac{\hbar}{m}\frac{d^2}{dx^2}\right)\psi \, dx = \frac{2}{\hbar}\int \psi^* \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi \, dx$$

$$= \frac{2}{\hbar}\langle T \rangle$$

$$\langle T \rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right)$$

Virijalni teorem za harmonički oscilator: $\langle T \rangle = \langle V \rangle$

17.5



Ukupni hamiltonijan za ovaj sistem glasi:

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{R}$$

Član $\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{R}$ predstavlja interakciju dva protona i on je konstantan. Stoga ga možemo u računu, koji slijedi izostaviti, a na kraju računa, jednostavno dodati energiji koju dobijemo za elektron.

Pretpostavljamo da probna funkcija za molekulsku valnu funkciju za osnovno stanje H_2^+ ima oblik ← bonding orbitala

$$\psi = A\left[u(r_1) + u(r_2)\right]$$

gdje je

$$u(r) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

Vidimo da $u(r)$ ima oblik valne funkcije osnovnog stanja za elektron u vodikovom atomu. Probna funkcija ψ je linearna kombinacija dvije atomske valne funkcije (ili atomske orbitale). Zato se ova metoda i zove LCAO, Linear Combination of Atomic Orbitals.

Ako je udaljenost između protona R nekoliko puta veća od Bohrovog radijusa a_0 (što ćemo potvrditi ovim računom!) tada je ψ dobra aproksimacija za pravu molekulsku valnu funkciju. Očekujemo da ako je elektron blizu, na primjer, jezgre 1 tada

$$\frac{1}{r_2} \ll \frac{1}{r_1}$$

pa $\frac{1}{r_2}$ u prvoj aproksimaciji možemo zanemariti u Hamiltonijanu. Valna funkcija je aproksimativno jednaka

$$\psi \sim A\, u(r_1)$$

Slično je ako se elektron nalazi blizu jezgre 2

$$\psi \sim A\, u(r_2)$$

pa je pretpostavljeni oblik od ψ logičan i opravdan.

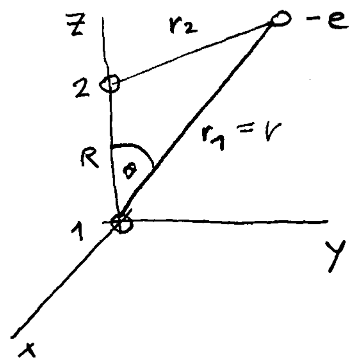
Normalizirajmo ψ

$$1 = \int \psi^* \psi \, d^3r = |A|^2 \left\{ \int |u(r_1)|^2 d^3r + \int |u(r_2)|^2 d^3r + 2 \int u(r_1) u(r_2) \, d^3r \right\}$$

Funkcija u već je normalizirana

$$\int |u(r_1)|^2 d^3r = \int |u(r_2)|^2 d^3r = 1$$

Kod računanja trećeg integrala u normalizaciji postavimo ishodište u protonu 1, a protonu 2 postavimo na z os



$$r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

Imamo,

$$J = \int u(r_1) u(r_2) \, d^3r = \int_0^{2\pi} d\varphi \int_0^{\infty} dr \cdot r^2 e^{-r/a_0} \int_0^{\pi} d\theta \sin\theta \cdot \frac{1}{\pi a_0^3} e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a_0}$$

$$y^2 = r^2 + R^2 - 2rR\cos\theta$$

$$2y\,dy = 2rR\sin\theta \, d\theta$$

$$J = e^{-R/a_0} \left[1 + \left(\frac{R}{a_0}\right) + \frac{1}{3}\left(\frac{R}{a_0}\right)^2 \right]$$

Konstanta normalizacije jednaka je

$$A^2 = \frac{1}{2(1+J)}$$

Sljedeći korak je računanje

$$\int \psi^* H \psi \, d^3r$$

Primijetimo da vrijedi

$$\left(-\frac{\hbar^2}{2m} \vec{\nabla}^2 - \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r_1} \right) u(r_1) = E_1 u(r_1)$$

pa je

$$H\psi = A\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0}\cdot\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right]\left[u(r_1)+u(r_2)\right] =$$

$$= \underline{AE_1 u(r_1)} - A\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{r_2}u(r_1) + \underline{AE_1 u(r_2)} - A\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{r_1}u(r_2)$$

$$= E_1\psi - A\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_2}u(r_1)+\frac{1}{r_1}u(r_2)\right)$$

Uvrstimo u $\langle\psi|H|\psi\rangle$

$$\int\psi^* H\psi = \int\psi^*\left\{E_1\psi - A\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_2}u(r_1)+\frac{1}{r_1}u(r_2)\right)\right\}d^3r =$$

$$= E_1 - 2|A|^2\frac{e^2}{4\pi\epsilon_0}\left[\int u(r_1)\frac{1}{r_2}u(r_1)d^3r + \int u(r_1)\frac{1}{r_1}u(r_2)d^3r\right]$$

Integrali u gornjoj jednakosti rješavaju se na isti način kao i integral J kod normalizacije. Uzmimo prvi integral

$$\int u(r_1)\frac{1}{r_2}u(r_1)d^3r = \int_0^{2\pi}d\varphi\int_0^{\infty}dr\cdot r^2\frac{1}{\pi a_0^3}e^{-2r/a_0}\int_0^{\pi}d\theta\sin\theta\cdot\frac{1}{\sqrt{r^2+R^2-2rR\cos\theta}}$$

$$y^2 = r^2+R^2-2rR\cos\theta$$

$$2y\,dy = +2rR\sin\theta\,d\theta$$

Integral po θ jednak je

$$\frac{1}{rR}\int_{|r-R|}^{R+r}dy\,y\cdot\frac{1}{y} = \frac{1}{rR}\left[(R+r)-|r-R|\right]$$

Ako označimo

$$D = a_0\int u(r_1)\frac{1}{r_2}u(r_1)d^3r$$

$$X = a_0\int u(r_1)\frac{1}{r_1}u(r_2)d^3r$$

za srednju vrijednost od H u stanju ψ dobijamo

$$\langle H \rangle = \left[1 + 2\,\frac{(D+X)}{(1+J)} \right] E_1$$

Na ovaj izraz dodajemo proton-proton interakciju koju smo izostavili na početku računa

$$\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{R} = -\frac{2a_0}{R} E_1 \quad \left(E_1 = -\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{2a_0} = -13{,}6\ \mathrm{eV} \right)$$

Za lakšu primjenu varijacijskog pristupa uvodimo oznake

$$\frac{\langle H \rangle}{(-E_1)} = F(x)$$

$$\frac{R}{a_0} = x$$

Funkcija kojoj tražimo minimum je [R, odnosno x je varijacijski parametar]

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{\left(1 - \frac{2}{3}x^2\right) e^{-x} + (1+x) e^{-2x}}{1 + \left(1 + x + \frac{1}{3}x^2\right) e^{-x}} \right\}$$

Za ravnotežnu udaljenost dobijemo

$$x_m = 2{,}49 \Rightarrow R_m = 2{,}49\, a_0$$

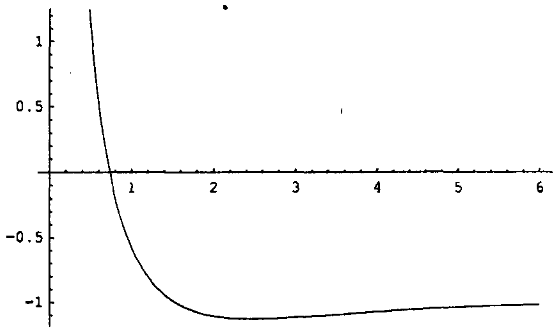
Za minimum od $F(x)$ dobijemo

$$F(x_m) = -1{,}13 \Rightarrow \langle H \rangle = 1{,}13 E_1 = -15{,}37\ \mathrm{eV}$$

Ukupna energija sustava: $-15{,}37\ \mathrm{eV}$

Energija vezanja: $-\left(\langle H \rangle - E_1\right) = 1{,}77\ \mathrm{eV}$

$$\text{Plot}\left[-1+\frac{2}{x}\left(\frac{(1-2/3\,x^2)\,\text{Exp}[-x]+(1+x)\,\text{Exp}[-2\,x]}{1+(1+x+1/3\,x^2)\,\text{Exp}[-x]}\right),\ \{x,\ 0.2,\ 6\}\right]$$



$$\text{D}\left[-1+\frac{2}{x}\left(\frac{(1-2/3\,x^2)\,\text{Exp}[-x]+(1+x)\,\text{Exp}[-2\,x]}{1+(1+x+1/3\,x^2)\,\text{Exp}[-x]}\right),\ x\right]$$

$$-\left(2\left(e^{-2x}(1+x)+e^{-x}\left(1-\frac{2x^2}{3}\right)\right)\left(e^{-x}\left(1+\frac{2x}{3}\right)-e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)\right)\Big/\left(x\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)^2\right)+$$
$$\frac{2\left(e^{-2x}-\frac{4e^{-x}x}{3}-2e^{-2x}(1+x)-e^{-x}\left(1-\frac{2x^2}{3}\right)\right)}{x\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)}-\frac{2\left(e^{-2x}(1+x)+e^{-x}\left(1-\frac{2x^2}{3}\right)\right)}{x^2\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)}$$

FindRoot[

$$-\left(2\left(e^{-2x}(1+x)+e^{-x}\left(1-\frac{2x^2}{3}\right)\right)\left(e^{-x}\left(1+\frac{2x}{3}\right)-e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)\right)\Big/\left(x\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)^2\right)+$$
$$\frac{2\left(e^{-2x}-\frac{4e^{-x}x}{3}-2e^{-2x}(1+x)-e^{-x}\left(1-\frac{2x^2}{3}\right)\right)}{x\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)}-\frac{2\left(e^{-2x}(1+x)+e^{-x}\left(1-\frac{2x^2}{3}\right)\right)}{x^2\left(1+e^{-x}\left(1+x+\frac{x^2}{3}\right)\right)}=0,$$

{x, 2}]

$\{x \to 2.49283\}$

$$\text{Function}\left[x,\ -1+\frac{2}{x}\left(\frac{(1-2/3\,x^2)\,\text{Exp}[-x]+(1+x)\,\text{Exp}[-2\,x]}{1+(1+x+1/3\,x^2)\,\text{Exp}[-x]}\right)\right][2.49282941865608]$$

-1.12966

17.5-5

$\boxed{17.6}$ Neka je probna funkcija $f(\vec{r})$. Ispitajmo slučaj $n=2$.

Poznata je valna funkcija $\psi_1(\vec{r})$. Formiramo stanje

$$|g\rangle = |f\rangle - |\psi_1\rangle\langle\psi_1|f\rangle \quad ; \quad \langle\psi_1|\psi_1\rangle = 1$$

Stanje $|g\rangle$ ortogonalno je na $|\psi_1\rangle$

$$\langle\psi_1|g\rangle = \langle\psi_1|f\rangle - \underbrace{\langle\psi_1|\psi_1\rangle}_{=1}\langle\psi_1|f\rangle = 0$$

Normaliziramo $|g\rangle$

$$\langle g|g\rangle = 1$$

$$\big(\langle f| - \langle f|\psi_1\rangle\langle\psi_1|\big)\big(|f\rangle - |\psi_1\rangle\langle\psi_1|f\rangle\big) = 1$$

$$\langle f|f\rangle - \underbrace{\langle f|\psi_1\rangle\langle\psi_1|f\rangle}_{|\langle f|\psi_1\rangle|^2} - \underbrace{\langle f|\psi_1\rangle\langle\psi_1|f\rangle}_{\text{isto}} + |\langle f|\psi_1\rangle|^2 = 1$$

$$\langle f|f\rangle - |\langle f|\psi_1\rangle|^2 = 1 \quad (*)$$

Ako je $|g\rangle$ normalizirano stanje mora zadovoljavati gornji uvjet.

Potražimo srednju vrijednost $\langle g|H|g\rangle$

$$\big(\langle f| - \langle f|\psi_1\rangle\langle\psi_1|\big) H \big(|f\rangle - |\psi_1\rangle\langle\psi_1|f\rangle\big) =$$

$$= \langle f|H|f\rangle - \langle f|\underbrace{H|\psi_1\rangle}_{E_1|\psi_1\rangle}\langle\psi_1|f\rangle - \langle f|\psi_1\rangle\underbrace{\langle\psi_1|H}_{E_1\langle\psi_1|}|f\rangle$$
$$+ \langle f|\psi_1\rangle\underbrace{\langle\psi_1|H|\psi_1\rangle}_{E_1}\langle\psi_1|f\rangle$$

Znamo da je

$$H|\psi_1\rangle = E_1|\psi_1\rangle$$

$$= \langle f|H|f\rangle - E_1|\langle f|\psi_1\rangle|^2$$

Također, ako je $\{|\psi_k\rangle\}$ potpun skup vrijedi

$$\sum_{k=1}^{\infty} |\psi_k\rangle\langle\psi_k| = 1$$

Zapis Hamiltonijana u toj bazi

$$H = \sum_{k=1}^{\infty} E_k |\psi_k\rangle\langle\psi_k|$$

Uz relaciju potpunosti uvjet normalizacije (*) glasi

$$\sum_{k=1}^{\infty} \langle f|\psi_k\rangle\langle\psi_k|f\rangle - |\langle f|\psi_1\rangle|^2 = \sum_{k=2}^{\infty} |\langle f|\psi_1\rangle|^2 = 1$$

Srednja vrijednost hamiltonijana u stanju $|g\rangle$ postaje

$$\langle g|H|g\rangle = \sum_{k=1}^{\infty} E_k |\langle f|\psi_k\rangle|^2 - E_1 |\langle f|\psi_1\rangle|^2$$

$$= \sum_{k=2}^{\infty} E_k |\langle f|\psi_k\rangle|^2 \geq E_2 \sum_{k=2}^{\infty} |\langle f|\psi_k\rangle|^2 = E_2$$

Dokazali smo sljedeće: ako uzmemo normaliziranu funkciju $g(\vec{r})$ oblika

$$g(\vec{r}) = f(\vec{r}) - \psi_1(\vec{r}) \cdot \int \psi_1^* f \, d^3r$$

gdje ψ_1 normalizirana, a f probna funkcija tada je srednja vrijednost od H u stanju $g(\vec{r})$ uvijek veća od E_2.

Generaliziramo: za proizvoljni n imamo

$$|g\rangle = |f\rangle - \sum_{k=1}^{n-1} |\psi_k\rangle\langle\psi_k|f\rangle$$

Normaliziramo

$$\langle g|g\rangle = 1$$

$$\left(\langle f| - \sum_{k=1}^{n-1} \langle f|\psi_k\rangle\langle\psi_k|\right)\left(|f\rangle - \sum_{k=1}^{n-1} |\psi_k\rangle\langle\psi_k|f\rangle\right) =$$

$$= \langle f|f\rangle - \sum_{k=1}^{n-1} |\langle f|\psi_k\rangle|^2 = 1$$

Uz

$$\sum_{k=1}^{\infty} |\psi_k\rangle\langle\psi_k| = 1$$

uvjet normalizacije stanja $|g\rangle$ postaje

$$\sum_{k=n}^{\infty} |\langle f|\psi_k\rangle|^2 = 1$$

Srednja vrijednost od H u stanju $|g\rangle$

$$\left(\langle f| - \sum_{k=1}^{n-1} \langle f|\psi_k\rangle\langle\psi_k|\right) H \left(|f\rangle - \sum_{k=1}^{n-1} |\psi_k\rangle\langle\psi_k|f\rangle\right)$$

$$= \langle f|H|f\rangle - \sum_{k=1}^{n-1} |\langle f|\psi_k\rangle|^2 E_k$$

$$= \sum_{k=1}^{\infty} E_k |\langle f|\psi_k\rangle|^2 - \sum_{k=1}^{n-1} |\langle f|\psi_k\rangle| E_k = \sum_{k=n}^{\infty} E_k |\langle f|\psi_k\rangle|^2 \geq$$

$$E_n \underbrace{\sum_{k=n}^{\infty} |\langle f|\psi_k\rangle|^2}_{=1} = E_n$$