# Kvantna mehanika2

Barbara Horvat

25.5.2005

*Metoda variacije in metoda Hartreeja-Focka, B1*

NAVODILO

Variacijsko določi energijo osnovnega stanja atoma $^6Li$. Pri nastavku za poskusno funkcijo upoštevaj rezultat naloge A1 in zasenčenje elektrona v $2s^1$.

REŠITEV

Imamo tri elektrone: dva v $1s$ orbitali in enega v $2s$ orbitali. Hamiltonjan je potem oblike:

$$H^{Li} = \frac{1}{2m}\vec{p_1}^2 + \frac{1}{2m}\vec{p_2}^2 + \frac{1}{2m}\vec{p_3}^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} + \frac{e^2}{|\vec{r}_2 - \vec{r}_1|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_1|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_2|} =$$

$$= H_1 + H_2 + H_3 + V_1 + V_2 + V_3 = H^{He} + H_3 + V_1 + V_2, \ kjer$$

$Z$ je število elektronov (3),
$H_i = \frac{1}{2m}\vec{p_i}^2 - \frac{Ze^2}{r_i}$, za $i = 1,2,3,$
$V_i = \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$, za $i,j,k = 1,2,3,$
$H^{He}$ je Hamiltonjan iz naloge A1 za $^4He$.

Variacijski nastavek je oblike:

$$|\psi>=|100>_1\,|100>_2\,|0,0>|200>_3, \ kjer$$

$|100>_i = \psi_{100}(r)_i = R_{10}(r)_i Y_{00}(\theta,\phi) = 2(\frac{Z^*}{a})^{\frac{3}{2}} e^{-\frac{Z^*}{a}r_i}\ \frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{\pi}}(\frac{Z^*}{a})^{\frac{3}{2}} e^{-\frac{Z^*}{a}r_i}$, kjer $i = 1,2$
$Z^* = Z - \frac{5}{16}$ senčitev med elektronoma iz orbitale $1s$ iz naloge A1,
$|200>_3 = \psi_{100}(r)_3 = R_{20}(r)_3 Y_{00}(\theta,\phi) = 2(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Zr_3}{2a})e^{-\frac{Z^`}{2a}r_3}\ \frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{\pi}}(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Zr_3}{2a})e^{-\frac{Z^`}{2a}r_3}$, kjer
$Z^`$ senčeni naboj za elektrone med orbitalama $1s$ ter $2s$ in je naš parameter,
$a$ Bohrov radij,
$|0,0>= \frac{1}{\sqrt{2}}(|\uparrow\downarrow> - |\downarrow\uparrow>)$ pa predstavlja spinski del valovne fukcije za elektrona v $1s$ orbitali.

Variacijski princip:

Vemo, da vedno velja: $E_0 \leq \frac{<\psi|H|\psi>}{<\psi|\psi>}$, kjer je $E_0$ energija osnovnega stanja.
Mi pa imamo seveda energijo odvisno od nekega parametra $\mu$ oz. $E(\mu) = \frac{<\psi(\mu)|H|\psi(\mu)>}{<\psi(\mu)|\psi(\mu)>}$. Tako funkcijo minimiziramo. Če je v $\mu_0$ minimum energije, potem dobimo zgornjo mejo za energijo osnovnega stanja, ki ga iščemo oz. $E_0 \leq E(\mu_0)$.

Iz naloge A1 vemo:
$\underline{<\psi|H^{He}|\psi>} = -2Ry(-Z^{*2} + 2ZZ^* - \frac{5}{8}Z^*)$,
kjer $Ry = \frac{e^2}{2a} = 13,6eV$ (v enotah glede na Hamiltonjan),
$\underline{<\psi|H_3|\psi>} =<\psi|\frac{1}{2m}\vec{p_3}^2 - \frac{Ze^2}{r_3} - \frac{Z^`e^2}{r_3} + \frac{Z^`e^2}{r_3}|\psi>=<200|\frac{1}{2m}\vec{p_3}^2 - \frac{Ze^2}{r_3} - \frac{Z^`e^2}{r_3} + \frac{Z^`e^2}{r_3}|200>=$
$= -Ry\frac{Z^{`2}}{4} + <200|\frac{e^2}{r_3}(Z^` - Z)|200>$,
kjer $<200|\frac{1}{2m}\vec{p_3}^2 - \frac{Z^`e^2}{r_3}|200>= -Ry\frac{Z^{`2}}{n^2}$, kjer $n = 4$

Torej moramo izračunati le še:

$$<200|\frac{e^2}{r_3}(Z^` - Z)|200>$$

$$<\psi|\frac{e^2}{|\vec{r}_3 - \vec{r}_{1,2}|}|\psi>=<200|<100|_{1,2}\frac{e^2}{|\vec{r}_3 - \vec{r}_{1,2}|}|100>_{1,2}|200>$$

Torej:

$\underline{< 200|\frac{e^2}{r_3}(Z^` - Z)|200 > =}$
$= \int\int\int r_3^2 dr_3 d\theta_3 \sin\theta_3 d\phi_3 \frac{1}{\sqrt{\pi}}(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Z^` r_3}{2a})e^{-\frac{Z^` r_3}{2a}}(\frac{e^2}{r_3}(Z^`\text{-}Z))\frac{1}{\sqrt{\pi}}(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Z^` r_3}{2a})e^{-\frac{Z^` r_3}{2a}} =$
$= \int\int\int r_3 dr_3 d\theta_3 \sin\theta_3 d\phi_3 \frac{1}{\pi}(\frac{Z^`}{2a})^3(1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}} e^2(Z^`\text{-}Z) =$
$= 4\pi\frac{1}{\pi}(\frac{Z^`}{2a})^3 e^2(Z^`\text{-}Z)\int r_3 dr_3(1 - \frac{Z^` r_3}{a} + \frac{Z^{`2} r_3^2}{4a^2})e^{-\frac{Z^` r_3}{a}} =$
$= \frac{1}{4}e^2\frac{Z^`}{a}(Z^` - Z) = \underline{\frac{1}{2}RyZ^`(Z^` - Z),}$

kjer smo integrirali po celem prostoru in upoštevali, da je $\int_0^\infty x^n e^{-ax}dx = \frac{\Gamma(n+1)}{a^{n+1}}$,

$< 200| < 100|_1 \frac{e^2}{|\vec{r}_3 - \vec{r}_1|}|100 >_1 |200 >=$
$= \int\int\int\int\int\int r_3^2 dr_3 d\theta_3 \sin\theta_3 d\phi_3 r_1^2 dr_1 d\theta_1 \sin\theta_1 d\phi_1$
$\frac{1}{\pi^2}(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Z^` r_3}{2a})e^{-\frac{Z^` r_3}{2a}}(\frac{Z^*}{a})^{\frac{3}{2}}e^{-\frac{Z^* r_1}{a}}\frac{e^2}{|\vec{r}_3 - \vec{r}_1|}(\frac{Z^*}{a})^{\frac{3}{2}}e^{-\frac{Z^* r_1}{a}}(\frac{Z^`}{2a})^{\frac{3}{2}}(1 - \frac{Z^` r_3}{2a})e^{-\frac{Z^` r_3}{2a}} =$
$= \frac{1}{\pi^2}\int\int\int\int\int\int r_3^2 dr_3 d\theta_3 \sin\theta_3 d\phi_3 r_1^2 dr_1 d\theta_1 \sin\theta_1 d\phi_1 (\frac{Z^` Z^*}{2a^2})^3(1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}}\frac{e^2}{|\vec{r}_3 - \vec{r}_1|}e^{-\frac{2Z^* r_1}{a}}$,
tu upoštevamo:
$\frac{1}{|\vec{r}_3 - \vec{r}_1|} = \frac{1}{\sqrt{r_3^2 + r_1^2 - 2r_1 r_3 \cos\Theta}} = \sum_n \frac{r_<^n}{r_>^{n+1}}P_n(\cos\Theta) = \frac{1}{r_3}\sum_n(\frac{r_1}{r_3})^n P_n(\cos\Theta)$,
kjer je $\Theta$ kot med vektorjema $\vec{r}_1$ ter $\vec{r}_3$

$\sum_{m=-l}^{l} Y_{lm}(\theta,\phi)Y_{lm}(\theta^`,\phi^`)^* = \frac{2l+1}{4\pi}P_l(\cos\Theta)$, kjer
$\cos\Theta = \cos\theta\cos\theta^` + \sin\theta\sin\theta^`\cos(\phi - \phi^`)$, kar
je za naš primer: $\theta, \phi = \theta_1, \phi_1$ oz. $\theta^`, \phi^` = \theta_2, \phi_2$

$Y_{lm}(\theta,\phi) = (-1)^{\frac{m+|m|}{2}}P_{l|m|}(\cos\theta)e^{im\phi}\sqrt{\frac{2l+1}{4\pi}\frac{(1-|m|)!}{(1+|m|)!}}$
$Y_{l0}(\theta,\phi) = P_l(\cos\theta)\sqrt{\frac{2l+1}{4\pi}}$
$Y_{00} = \frac{1}{\sqrt{4\pi}}$
$P_{l0}(\xi) = P_l(\xi)$

$\int_0^\pi d\theta\sin\theta\int_0^{2\pi} d\phi Y_{lm}(\theta,\phi)^* Y_{l^` m^`}(\theta,\phi) = \delta_{ll^`}\delta_{mm^`}$
$r_3 > r_{1,2}$

Torej:
$\underline{< 200| < 100|_1 \frac{e^2}{|\vec{r}_3 - \vec{r}_1|}|100 >_1 |200 > =}$
$= \frac{1}{\pi^2}(\frac{Z^` Z^*}{2a^2})^3 e^2\int\int\int\int\int\int r_3^2 dr_3 d\theta_3 \sin\theta_3 d\phi_3 r_1^2 dr_1 d\theta_1 \sin\theta_1 d\phi_1 (1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}} e^{-\frac{2Z^* r_1}{a}}\frac{1}{r_3}\sum_n(\frac{r_1}{r_3})^n P_n(\cos\Theta) =$
$= \frac{1}{\pi^2}(\frac{Z^` Z^*}{2a^2})^3 e^2\int\int\int\int\int\int r_3^2 dr_3 d\theta_3 \sin\theta_3 d\phi_3 r_1^2 dr_1 d\theta_1 \sin\theta_1 d\phi_1 (1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}} e^{-\frac{2Z^* r_1}{a}}\frac{1}{r_3}\sum_{n=0}^\infty(\frac{r_1}{r_3})^n\frac{4\pi}{2n+1}$
$\sum_{m=-n}^{n} Y_{nm}(\theta,\phi)Y_{nm}(\theta^`,\phi^`)^* =$
$= \frac{4\pi}{\pi^2}(\frac{Z^` Z^*}{2a^2})^3 e^2\sum_{n=0}^\infty\sum_{m=-n}^{n}\int r_1^2 dr_1\int r_3^2 dr_3\int\sin\theta_1 d\theta_1\int d\phi_1\int\sin\theta_3 d\theta_3\int d\phi_3(1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}} e^{-\frac{2Z^* r_1}{a}}\frac{1}{r_3}(\frac{r_1}{r_3})^n$
$\frac{4\pi}{2n+1}Y_{00}^*(\theta_1,\phi_1)Y_{nm}(\theta_1,\phi_1)Y_{nm}^*(\theta_3,\phi_3)Y_{00}(\theta_3,\phi_3) =$
$= \frac{4}{\pi}(\frac{Z^` Z^*}{2a^2})^3 e^2\int r_1^2 dr_1\int r_3^2 dr_3(1 - \frac{Z^` r_3}{2a})^2 e^{-\frac{Z^` r_3}{a}} e^{-\frac{2Z^* r_1}{a}}\frac{1}{r_3}4\pi =$
$= 16(\frac{Z^` Z^*}{2a^2})^3\frac{e^2}{8}\int r_1^2 dr_1\int r_3 dr_3(1 - \frac{Z^` r_3}{a} + (\frac{Z^` r_3}{2a})^2)e^{-\frac{Z^` r_3}{a}} e^{-\frac{2Z^* r_1}{a}} =$
$= 2e^2(\frac{Z^` Z^*}{2a^2})^3\int_0^\infty r_1^2 dr_1 e^{-\frac{2Z^* r_1}{a}}\int_0^\infty(r_3 - \frac{Z^`}{a}r_3^2 + (\frac{Z^`}{2a})^2 r_3^3)e^{-\frac{Z^` r_3}{a}} =$
$= \frac{1}{4}e^2\frac{Z^`}{a} = \underline{\frac{1}{2}RyZ^`}$

Ko vse skupaj sestavimo skupaj in upoštevamo še $Z^* = Z - \frac{5}{16}$, dobimo:

$$< \psi|H^{Li}|\psi >= Ry(-2(Z - \frac{5}{16})^2 + \frac{1}{4}Z^{`2} - \frac{1}{2}ZZ^` + Z^`).$$

Ta rezultat variiramo po $Z^`$ in poiščemo minimum, ki je enak: $Z_0^` = Z - 2$.

Torej za energijo osnovnega stanja dobimo:

$$E_0^{Li} =< \psi|H|\psi > |_{Z^` = Z_0^`} = Ry(-2(Z - \frac{5}{16})^2 + \frac{1}{2}(Z - 2)(1 - \frac{Z}{2})).$$

Vemo, da je za $Li$ $Z = 3$, tako da je $E_0 \sim -200eV$.