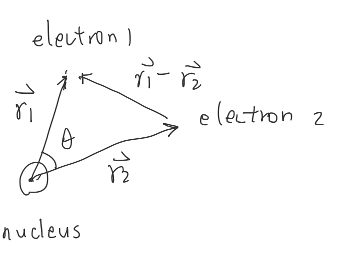
SQ 14, 15

2021年2月28日 星期日 下午3:52

SQ 14.

We use 1st-order perturbation theory to estimate the ground state energy of He-atom.



The Hamiltonian of He-atom:

$$\hat{H} = \underbrace{\underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}}_{\hat{h}_1} \underbrace{- \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{h}_2}}_{\hat{H}_0} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\hat{H}'},$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$.

The ground state wavefunction for the unperturbed term $\hat{H}_0$ is:

$$\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) = \left(\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Z}{a_0}r_1}\right)\left(\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Z}{a_0}r_2}\right),$$

where $Z = 2$ for He-atom.

(a) We estimate the 0-th order energy $E^{(0)}$:

$$E^{(0)} = \iint \phi_{1s}^*(\vec{r}_1)\,\phi_{1s}^*(\vec{r}_2)\,\hat{H}_0\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2$$

$$= \int \phi_{1s}^*(\vec{r}_1)\,\hat{h}_1\,\phi_{1s}(\vec{r}_1)\,d^3r_1 + \int \phi_{1s}^*(\vec{r}_2)\,\hat{h}_2\,\phi_{1s}(\vec{r}_2)\,d^3r_2$$

$$= Z^2E_1 + Z^2E_1$$

$$= 8E_1 = -108.8\,eV = -4\,Eh,$$

where $E_1 = -13.6\,eV$ is the ground state energy of H-atom.

(b) We estimate the 1st-order energy $E^{(1)}$:

$$E^{(1)} = \iint \phi_{1s}^*(\vec{r}_1)\,\phi_{1s}^*(\vec{r}_2)\,\hat{H}'\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2$$

$$= \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^6 \frac{e^2}{4\pi\varepsilon_0}\int e^{-\frac{2Z}{a_0}r_2}\underbrace{\left(\int e^{-\frac{2Z}{a_0}r_1}\frac{1}{|\vec{r}_1-\vec{r}_2|}\,d^3r_1\right)}_{I} d^3r_2$$

$d^3r_2 = r_2^2\sin\theta\,dr_2\,d\theta\,d\phi$

We first evaluate the inner integral I:

$$I = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-\frac{2Z}{a_0}r_1}\frac{1}{(r_1^2+r_2^2-2r_1r_2\cos\theta)^{\frac{1}{2}}}\,r_1^2\sin\theta\,dr_1\,d\theta\,d\phi$$

($\sin\theta\,d\theta \to d(\cos\theta)$)

the angel θ is the angle between $\vec{r}_1$ and $\vec{r}_2$ and we fix $\vec{r}_2$ here and put it in z-direction and integrate over $\vec{r}_1$.

$$= 2\pi\int_0^{\infty} e^{-\frac{2Z}{a_0}r_1}\,r_1^2\left[\left(-\frac{1}{2r_1r_2}\right)(-2)\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{\frac{1}{2}}\right]_0^{\pi} dr_1$$

(2π: ϕ part integral; bracket: θ part integral)

$$= 2\pi\int_0^{\infty} e^{-\frac{2Z}{a_0}r_1}\,\frac{r_1}{r_2}\left(r_1+r_2-|r_1-r_2|\right)dr_1$$

($r_1+r_2-|r_1-r_2| = \sqrt{(r_1+r_2)^2}-\sqrt{(r_1-r_2)^2}$)

We separate the integral into two parts $r_1>r_2$ and $r_1<r_2$:

$$I = 2\pi\left(\int_{r_2}^{\infty} e^{-\frac{2Z}{a_0}r_1}(2r_1)\,dr_1 + \int_0^{r_2} e^{-\frac{2Z}{a_0}r_1}\left(\frac{2r_1^2}{r_2}\right)dr_1\right)$$

$r_1>r_2$: $r_1+r_2-|r_1-r_2| = 2r_2$ $\qquad$ $r_1<r_2$: $r_1+r_2-|r_1-r_2| = 2r_1$

$$= 2\pi\left(-\frac{1}{2}\left(\frac{a_0}{Z}\right)^2 e^{-\frac{2Z}{a_0}r_2} + \frac{1}{2}\left(\frac{a_0}{Z}\right)^3\frac{1}{r_2} - \frac{1}{2}\left(\frac{a_0}{Z}\right)^3\frac{1}{r_2}e^{-\frac{2Z}{a_0}r_2}\right)$$

(We do this step by integration by parts. And we have used the formula $\int_0^{\infty} e^{-\beta x}x^n\,dx = \frac{1}{\beta^{n+1}}n!$)

Then we go back to evaluate $E^{(1)}$:

the θ,ϕ part integral of r_2: $\int_0^{2\pi}\int_0^{\pi}\sin\theta\,d\theta\,d\phi = 4\pi$

$$E^{(1)} = \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^6\frac{e^2}{4\pi\varepsilon_0}(4\pi)\int_0^{\infty}2\pi\left(-\frac{1}{2}\left(\frac{a_0}{Z}\right)^2 r_2^2\,e^{-\frac{4Z}{a_0}r_2} + \frac{1}{2}\left(\frac{a_0}{Z}\right)^3 r_2\,e^{-\frac{2Z}{a_0}r_2} - \frac{1}{2}\left(\frac{a_0}{Z}\right)^3 r_2\,e^{-\frac{4Z}{a_0}r_2}\right)dr_2$$

$$= 8\left(\frac{Z}{a_0}\right)^6\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{2}\left(\frac{a_0}{Z}\right)^2\left(\frac{a_0}{4Z}\right)^3 2! + \frac{1}{2}\left(\frac{a_0}{Z}\right)^3\left(\frac{a_0}{2Z}\right)^2 - \frac{1}{2}\left(\frac{a_0}{Z}\right)^3\left(\frac{a_0}{4Z}\right)^2\right)$$

$$= \frac{5}{8}Z\,\frac{e^2}{4\pi\varepsilon_0 a_0}$$

$$= \frac{5}{8}Z\,(Eh) = \frac{5}{4}Eh, \quad \text{where } Z = 2$$

(c) Our estimated He-atom ground state energy is

$$E^{(0)} + E^{(1)} = -4\,Eh + \frac{5}{4}Eh = -2.75\,Eh,$$

which is close to the experimental value $-2.9033\,Eh$. And the estimated energy by perturbation theory is higher than the true value.

SQ 15.

We use the variational method to estimate the ground state energy of He-atom, with the trial wavefunction:

$$\psi_{trial}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{\frac{3}{2}} e^{-\frac{\zeta}{a_0}r_1}\,\frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{\frac{3}{2}} e^{-\frac{\zeta}{a_0}r_2},$$

which is normalized.

(a) We rewrite the Hamiltonian of He-atom as:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\varepsilon_0 r_1}}_{\hat{H}_1} \underbrace{- \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\varepsilon_0 r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\hat{H}'} \underbrace{- \frac{(2-\zeta)e^2}{4\pi\varepsilon_0 r_1}}_{\hat{h}_1} \underbrace{- \frac{(2-\zeta)e^2}{4\pi\varepsilon_0 r_2}}_{\hat{h}_2},$$

which can simplify our calculation.

Then

$$\langle\hat{H}\rangle = \langle\psi_{trial}(\vec{r}_1,\vec{r}_2)|\hat{H}|\psi_{trial}(\vec{r}_1,\vec{r}_2)\rangle$$

$$= \langle\hat{H}_1\rangle + \langle\hat{H}_2\rangle + \langle\hat{H}'\rangle + \langle\hat{h}_1\rangle + \langle\hat{h}_2\rangle,$$

(1) $\langle\hat{H}_1\rangle$ and $\langle\hat{H}_2\rangle$ can be treated as Hydrogen-like atom with $Z = \zeta$: $\langle\hat{H}_1\rangle = \langle\hat{H}_2\rangle = \zeta^2(-13.6\,eV) = -\frac{1}{2}\zeta^2\,Eh$.

(2) Replace Z by ζ, we have done the integral $\langle\hat{H}'\rangle$ in SQ14.

$$\Rightarrow \langle\hat{H}'\rangle = \frac{5}{8}\zeta\,Eh.$$

(3) We evaluate $\langle\hat{h}_1\rangle$ and $\langle\hat{h}_2\rangle$:

$$\langle\hat{h}_1\rangle = -\frac{(2-\zeta)e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r_1}\right\rangle$$

$$= -\frac{(2-\zeta)e^2}{4\pi\varepsilon_0}(4\pi)\int_0^{\infty}\frac{1}{\pi}\left(\frac{\zeta}{a_0}\right)^3 e^{-\frac{2\zeta}{a_0}r_1}\frac{1}{r_1}\,dr_1$$

(4π: θ,ϕ part integral)

$$= -\frac{(2-\zeta)e^2}{4\pi\varepsilon_0}\,4\left(\frac{\zeta}{a_0}\right)^3\left(\frac{a_0}{2\zeta}\right)^2 \quad \left(\text{again by } \int_0^{\infty}e^{-\beta x}x^n\,dx = \frac{1}{\beta^{n+1}}n!\right)$$

$$= -\zeta(2-\zeta)\frac{e^2}{4\pi\varepsilon_0 a_0} = \zeta(\zeta-2)\,Eh.$$

And obviously $\langle\hat{h}_2\rangle = \langle\hat{h}_1\rangle = \zeta(\zeta-2)\,Eh$.

Therefore, $\langle\hat{H}\rangle = -\zeta^2\,Eh + 2\zeta(\zeta-2)\,Eh + \frac{5}{8}\zeta\,Eh \qquad (1)$

In atomic unit: $\langle\hat{H}\rangle = -\zeta^2 + 2\zeta(\zeta-2) + \frac{5}{8}\zeta \qquad (Eh=1)$

(b) By variational method,

$$\frac{\partial\langle\hat{H}\rangle}{\partial\zeta} = -2\zeta + 4\zeta - 4 + \frac{5}{8} = 2\zeta - \frac{27}{8} = 0$$

$$\Rightarrow \zeta = 1.6875,$$

where ζ can be viewed as the effective charge of one electron influenced by the nucleus and the other electron.

Replace $\zeta = 1.6875$ into eqn. (1), we get

$$\langle\hat{H}\rangle_{min} \approx -2.848\,Eh,$$

which is close to but slightly higher than the experimental value $-2.9033\,Eh$ as expected in variational method.