Variational Method

any normalized wavefunction \( \langle \psi | \psi \rangle = 1 \)

\[ E_{gs} \leq \langle \psi | H | \psi \rangle \]

\[ \psi = \sum_n c_n \psi_n \quad H \psi_n = E_n \psi_n \]

\[ 1 = \langle \psi | \psi \rangle = \langle \sum_n c_n \psi_n | \sum_n c_n \psi_n \rangle \]

\[ = \sum_n \sum_m c_n^* c_m \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 \]

\[ \langle \psi | H | \psi \rangle = \langle \sum_n c_n \psi_n | H | \sum_n c_n \psi_n \rangle \]

\[ = \sum_n \sum_m c_n^* c_m E_m \langle \psi_m | \psi_n \rangle \]

\[ = \sum_n |c_n|^2 E_n \geq E_{gs} \sum_n |c_n|^2 = E_{gs} \]
\[ H = \frac{1}{2m r^2} \frac{d}{du} \frac{d}{dv} + \frac{\hbar^2 l(l+1)}{2m r^2} \neq -\frac{\hbar c}{r} \]

\[ l = 0 \quad 4 = R(\nu) Y_0^0 \quad R(\nu) = A e^{-\nu r} \]

\[ \int_0^\infty r^2 R^2 dr = A^2 \int_0^\infty e^{-2\nu r} r^2 dr = A^2 \frac{2}{(2\nu)^3} = 1 \]

\[ A^2 = \frac{86^3}{2} \]

\[ \frac{dR}{dv} = -bA e^{-\nu r} \quad \frac{d}{dv} R = -bA e^{-\nu r} \left( 2b - b^2 r^2 \right) \]

\[ \langle \psi_1 \psi_1 \psi_1 \psi_1 \rangle = A^2 \int_0^\infty dr \, r^2 \left( \frac{\hbar^2}{2m r^2} \right) \left( -b(2b - b^2 r^2) - \frac{\hbar c}{r} \right) e^{-2\nu r} \]

\[ = \frac{46^3}{2} \int_0^\infty \frac{dr}{dv} e^{-2\nu r} \left( \frac{b^2}{2m} \left( 2b^2 - b^2 r^2 \right) - \frac{\hbar c}{r} \right) \]

\[ = \frac{46^3}{2} \left[ \frac{b^2}{2m} \left( \frac{2b^2}{(2b)^2} - \frac{b^2}{(2b)^3} - \frac{\hbar c}{(2b)^2} \right) \right] \]

\[ = \frac{46^3}{2} \left( \frac{b^2}{2m} \left( \frac{1}{26} - \frac{1}{46} \right) - \frac{\hbar c}{46^2} \right) \]

\[ = \frac{5}{2m} b^2 - \frac{\hbar c}{46^2} \]

\[ \frac{d}{db} \langle \psi_1 \psi_1 \psi_1 \psi_1 \rangle = \frac{b^2}{m} - \frac{\hbar c}{b} = 0 \]

\[ b = \frac{\alpha m c}{\hbar^2} \]

\[ \langle \psi_1 \psi_1 \psi_1 \psi_1 \rangle = \frac{b^2}{2m} \left( \frac{\alpha m c}{\hbar^2} \right)^2 - \frac{\hbar c}{b} \left( \frac{\alpha m c}{\hbar^2} \right) = -\frac{\alpha^2 m c^2}{Z} \]

\[ = -13.6 \text{ eV} \quad \text{gauge} \quad \Rightarrow \quad -11 \text{ eV} \]
\[ H = -\frac{\hbar^2}{2m} (\nabla^2 + \mathbf{r}_2^2) - \hbar c \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right) \]

1st order pert.
\[ E_{gs} = -78.775 \text{ eV} \]

1st order pert.
\[ E_{gs} = -75 \text{ eV} \]

Hydrogen
\[ \psi_{1s} = \frac{2^{3/2}}{\pi^{1/2}} e^{-2\sqrt{r}} \]

\[ \psi_0 = \psi_{1s0} (r_1) \psi_{1s0} (r_2) = \frac{2^3}{\pi^{1/2}} e^{-2(r_1 + r_2)} \]

\[ H = -\frac{\hbar^2}{2m} (\nabla^2 + \mathbf{r}_2^2) - \hbar c \left( \frac{2}{r_1} + \frac{2}{r_2} \right) + \hbar c \left( \frac{2-2}{r_1} + \frac{2-2}{r_2} + \frac{1}{|r_1 - r_2|} \right) \]

\[ \langle \psi_0 | H | \psi_0 \rangle = 2 \frac{Z^2}{a} E_1 + 2(2-2) \hbar c \langle \psi_{1s0} | \hbar c | \psi_{1s0} \rangle + \langle \psi_0 | V_{ee} | \psi_0 \rangle \]

\[ \langle \psi_0 | \psi_{1s0} | \psi_0 \rangle = \frac{2}{a} \]

\[ 2(2-2) \hbar c \langle \psi_{1s0} | \psi_{1s0} \rangle = 2(2-2) \hbar c \frac{2}{a} \]

\[ = 2Z(2-2)(-2E_1) \]

\[ = -4Z(2-2)E_1 \]
\langle \psi_2 | V_{ee} | \psi_0 \rangle = 4 \pi a^2 \int \frac{e^{-2 \pi (r_1 + r_2)/a}}{1 - \frac{r_1 + r_2}{a}} \, dr_1 \, dr_2 \int e^{-2 \pi r_1/a} \, dr_1 \, dr_2

\frac{1}{|r_1 - r_2|} = \sqrt{(r_1 - r_2 \cos \theta_2)^2 + r_2^2 \sin^2 \theta_2}

= \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}

I_2 = \int e^{-2 \pi r_1/a} \, dr_1 \int e^{-2 \pi r_2/a} \, dr_2 \int e^{-2 \pi r_2/a} \, dr_2 \int e^{-2 \pi r_2/a} \, dr_2

= \int_0^\pi d\phi \int_0^\pi \sin \theta d\theta \int_0^{\infty} r_2^2 e^{-2 \pi r_2/a} \, dr_2 \int_0^{\infty} dx \, \frac{1}{\sqrt{x}} \frac{1}{2 \pi r_2}

= 2\pi \int_0^\pi d\phi \int_0^{\infty} dx \, \frac{1}{\sqrt{x}} \frac{1}{2 \pi r_2}

\int_0^{(r_1 + r_2)^2} \frac{(r_1 + r_2)^2}{(r_1 - r_2)^2}

\int_0^{(r_1 - r_2)^2} \frac{(r_1 + r_2)^2}{(r_1 - r_2)^2}

= 2\pi \int_0^\pi d\phi \int_0^{\infty} dx \, \frac{1}{\sqrt{x}} \frac{1}{2 \pi r_2}

\int_0^{(r_1 + r_2)^2} \frac{(r_1 + r_2)^2}{(r_1 - r_2)^2}

\int_0^{(r_1 - r_2)^2} \frac{(r_1 + r_2)^2}{(r_1 - r_2)^2}

= 4\pi \left( \int_0^{r_1} \frac{r_2^2}{r_1} e^{-2 \pi r_2/a} \, dr_2 + \int_0^{r_2} \frac{r_2^2}{r_2} e^{-2 \pi r_2/a} \, dr_2 \right)

= \frac{4 \pi a^3}{r_1 \, 2^3} \left( 1 - \left( 1 + \frac{r_1 + r_2}{a} \right) e^{-2 \pi r_2/a} \right)
\[ \langle \text{Vec} \rangle = \frac{h \alpha c}{\pi^2 \alpha^6} \int \frac{e^{-\frac{2 \pi r_i \alpha}{c^3}}}{1 + \frac{r_i \alpha}{c^3}} \frac{r_i}{v} \, dr_i = \frac{5}{8} \frac{h \alpha c}{\alpha} = -\frac{5}{4} \]

\[ \langle \frac{d}{dE} \rangle = 2 \frac{2 - 2}{4} = \frac{2 - 2}{4} = 0 \]

\[ \langle \frac{d}{dE} \rangle = \left( -4 \frac{27}{4} \right) E = \frac{2 - 2}{4} = 0 \]

\[ 2 = \frac{2 - 2}{4} = 1.6 \]

\[ \langle \frac{d}{dE} \rangle = \frac{1}{2} (\frac{3}{2}) E = -77.5 \text{ eV} \]

within 2%
Hydrogen Molecule Ion

\[
H = -\frac{\hbar^2 \rho^2}{2m} - \frac{1}{\hbar c} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad H_{pp} = \frac{1}{\hbar c}
\]

\[
\mathcal{L}_{C A O} \quad \psi = A \left( \psi_0 (r_1) + \psi_0 (r_2) \right)
\]

\[
\psi_0 (r) = \frac{1}{\sqrt{\pi \alpha^3}} e^{-r \alpha}
\]

\[
I = \frac{1}{\pi \alpha^3} \int e^{-r \alpha} e^{-\frac{\sqrt{r^2 + k^2} - 2r \rho \cos \Theta}{2 \rho}} r^2 \sin \Theta \, d\Theta \, d\phi \, dr
\]

\[
y = \sqrt{r^2 + k^2 - 2r \rho \cos \Theta} \quad d(y^2) = 2y dy = 2\rho \sin \Theta \, \rho \sin \Theta d\Theta
\]

\[
\int_0^{\pi} e^{-y^2} \sin \Theta \, d\Theta = \frac{1}{K^2} \int_{y^1}^{y^2} e^{-y^2} y \, dy
\]

\[
= -\frac{\alpha}{\hbar \rho} \left( e^{-(r+\rho/\alpha)(r+\rho/\alpha)} - e^{-(1-r/\rho)(1-r/\rho)} \right)
\]
\[
I = \frac{2 \pi}{\pi a^3} \frac{a}{R} \left( e^{-\frac{R}{a}} \int_0^\infty (v + R + a) e^{-\frac{2v}{a}} \, dv + \int_0^R (R - v + a) \, dv \right) + e^{-\frac{R}{a}} \int_0^\infty (v - R + a) e^{-\frac{2v}{a}} \, dv
\]

\[
= e^{-\frac{R}{a}} \left( 1 + \frac{R}{a} + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right) \quad \left( R \to \infty, \ I \to 0 \right)
\]

\[
I = |A|^2 \left( 1 + 2I + I^2 \right)
\]

\[
|A|^2 = \frac{1}{2(1 + I)}
\]

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial v^2} - \frac{\hbar \sigma c}{v} \right) \psi(v) = E, \quad \psi(v) = \psi_0(v)
\]

\[
H \psi = A \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial v^2} - \frac{\hbar \sigma c}{v} \right) \left( \frac{1}{v_1} + \frac{1}{v_2} \right) \left( \psi_0(v_1) + \psi_0(v_2) \right)
\]

\[
= E \psi - A \frac{\hbar \sigma c}{r} \left( \frac{1}{v_2} \psi_0(v_1) + \frac{1}{v_1} \psi_0(v_2) \right)
\]

\[
\langle \psi | H + H | \psi \rangle = E - |A|^2 \frac{\hbar \sigma c}{r} \left( \langle \psi_0 | \frac{1}{v_2} | \psi_0(v_1) \rangle + \langle \psi_0(v_1) | \frac{1}{v_2} | \psi_0 \rangle \right) + \langle \psi_0(v_2) | \frac{1}{v_2} | \psi_0(v_1) \rangle + \langle \psi_0(v_1) | \frac{1}{v_2} | \psi_0 \rangle
\]

\[
= E - 2|A|^2 \frac{\hbar \sigma c}{r} \left( \langle \psi_0(v_1) | \frac{1}{v_2} | \psi_0(v_1) \rangle + \langle \psi_0(v_2) | \frac{1}{v_2} | \psi_0 \rangle \right)
\]
\[ D = a \left< \frac{\psi_0 (r_1) \hat{r}_1 \cdot \hat{r}_2}{r_1 r_2} \right> \quad \text{direct} \]

\[ X = a \left< \frac{\psi_0 (r_1) \hat{r}_1 \cdot \hat{r}_2}{r_1 r_2} \right> \quad \text{exchange} \]

\[ D = \frac{a}{R} - (1 + \frac{a}{R}) e^{-\frac{2R}{a}} \]

\[ X = \left( 1 + \frac{R}{a} \right) e^{-\frac{R}{a}} \]

\[ E_i = -\frac{\alpha^2 m c^2}{2} = -\frac{\hbar \alpha c}{2} \]

\[ \left< \psi \right| H \left| \psi \right> = E_i - 2 \left| A \right|^2 \left( -2a E_i \right) \left( \frac{D + X}{a} \right) \]

\[ H_{\text{eff}} = \frac{\hbar \alpha c}{R} = -\frac{2a E_i}{R} \]

\[ \text{equilibrium} \quad R = 2.4 a = 1.3 \text{Å} \]

\[ \text{exp} \quad 1.06 \text{Å} \]