H_2 in a minimal basis

EXERCISE:

(1) Show that the Hamiltonian matrix for H_2 can be written in the basis of the two single-determinant states $|1\sigma_g^\alpha 1\sigma_g^\beta\rangle$ and $|1\sigma_u^\alpha 1\sigma_u^\beta\rangle$ as follows,

$$[\hat{H}] = \left[\begin{array}{cc} E_g & K \\ K & E_u \end{array}\right], \quad \text{where}$$

for $i = g, u, \quad E_i = 2h_{ii} + \langle 1\sigma_i 1\sigma_i | 1\sigma_i 1\sigma_i \rangle, \quad h_{ii} = \langle 1\sigma_i | \hat{h} | 1\sigma_i \rangle, \quad K = \langle 1\sigma_u 1\sigma_u | 1\sigma_g 1\sigma_g \rangle.$

(2) In the following, we use the minimal basis consisting of the two $1s$ atomic orbitals. Explain why, in the dissociation limit, $E_g = E_u$ and $K = \frac{1}{2}\langle 1s1s|1s1s\rangle > 0$.

(3) Conclude that, in the dissociation limit, the ground state is multiconfigurational and does correspond to two neutral hydrogen atoms with energy $E_g - K$.

H_2 - minimal basis - Dissociation limit

$//H_2$ dis

(1) . $[\hat{H}] = \begin{bmatrix} E_g & K \\ K & E_u \end{bmatrix}$

where $E_g = \langle 1\sigma_g^2 | \hat{H} | 1\sigma_g^2 \rangle$, $E_u = \langle 1\sigma_u^2 | \hat{H} | 1\sigma_u^2 \rangle$

$K = \langle 1\sigma_g^2 | \hat{H} | 1\sigma_u^2 \rangle$

- For a single determinant Φ,

$$\langle \Phi | \hat{H} | \Phi \rangle = 2\sum_i h_{ii} + \sum_{i,j} \left(2\langle ij|ij\rangle - \langle ij|ji\rangle \right)$$

where i,j are the doubly-occupied orbitals in Φ.

Therefore $E_g = 2h_{gg} + 2\langle 1\sigma_g 1\sigma_g | 1\sigma_g 1\sigma_g \rangle - \langle 1\sigma_g 1\sigma_g | 1\sigma_g 1\sigma_g \rangle$

$\boxed{E_g = 2h_{gg} + \langle 1\sigma_g 1\sigma_g | 1\sigma_g 1\sigma_g \rangle}$ with $h_{gg} = \langle 1\sigma_g | \hat{h} | 1\sigma_g \rangle$

- Similarly, $\boxed{E_u = 2h_{uu} + \langle 1\sigma_u 1\sigma_u | 1\sigma_u 1\sigma_u \rangle}$ with $h_{uu} = \langle 1\sigma_u | \hat{h} | 1\sigma_u \rangle$

- $\hat{H} = \hat{h} + \hat{W}_{ee}$ where $\hat{h} = \sum_{pq} h_{pq} \hat{E}_{pq}$ ← one-electron operator

Since $|1\sigma_g^2\rangle$ and $|1\sigma_u^2\rangle$ differ by a double excitation, $\langle 1\sigma_g^2 | \hat{h} | 1\sigma_u^2 \rangle = 0$

$\Rightarrow K = \langle 1\sigma_g^2 | \hat{W}_{ee} | 1\sigma_u^2 \rangle$ with $\hat{W}_{ee} = \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle \left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps} \right)$

$$= \frac{1}{2} \sum_{pqrs} \langle pr|qs\rangle \underbrace{\left(\sum_{\tau_1,\tau_2} \hat{a}^\dagger_{p,\tau_1} \hat{a}^\dagger_{r,\tau_2} \hat{a}_{s,\tau_2} \hat{a}_{q,\tau_1} \right)}_{\hat{e}_{pqrs}}$$

$$\langle 1\sigma_g^2 | \hat{e}_{pqrs} | 1\sigma_u^2 \rangle = \sum_{\tau_1\tau_2} \langle 1\sigma_g^2 | \hat{a}^\dagger_{p,\tau_1} \hat{a}^\dagger_{r,\tau_2} \hat{a}_{s,\tau_2} \hat{a}_{q,\tau_1} | 1\sigma_u^2 \rangle \quad (1)$$

in Eq. (1) $p \to \sigma_g$, $r \to \sigma_g$, $q \to \sigma_u$, $s \to \sigma_u$, otherwise we obtain zero.

Simplified notations: $1\sigma_g \equiv \sigma_g$ and $1\sigma_u \equiv \sigma_u$

We now have to simplify

$$\langle 1\sigma_g^2 | \hat{a}^\dagger_{\sigma_g,\tau_1} \hat{a}^\dagger_{\sigma_g,\tau_2} \hat{a}_{\sigma_u,\tau_2} \hat{a}_{\sigma_u,\tau_1} | 1\sigma_u^2 \rangle = C \quad (2)$$

- $\hat{a}_{\sigma_u,\tau_2} \hat{a}_{\sigma_u,\tau_1} | 1\sigma_u^2 \rangle = \hat{a}_{\sigma_u,\tau_2} \hat{a}_{\sigma_u,\tau_1} \hat{a}^\dagger_{\sigma_u,\alpha} \hat{a}^\dagger_{\sigma_u,\beta} |vac\rangle$

$= \delta_{\tau_1,\alpha} \hat{a}_{\sigma_u,\tau_2} \hat{a}^\dagger_{\sigma_u,\beta} |vac\rangle - \hat{a}_{\sigma_u,\tau_2} \hat{a}^\dagger_{\sigma_u,\alpha} \hat{a}_{\sigma_u,\tau_1} \hat{a}^\dagger_{\sigma_u,\beta} |vac\rangle$

$= \delta_{\tau_1\alpha} \delta_{\tau_2\beta} |vac\rangle - \delta_{\tau_1\beta} \delta_{\tau_2\alpha} |vac\rangle.$

- Similarly

$\hat{a}_{\sigma_g,\tau_2} \hat{a}_{\sigma_g,\tau_1} | 1\sigma_g^2 \rangle$

$= \left(\delta_{\tau_1,\alpha} \delta_{\tau_2\beta} - \delta_{\tau_1\beta} \delta_{\tau_2\alpha} \right) |vac\rangle$

$$C = \langle \hat{a}_{\sigma_g,\tau_2} \hat{a}_{\sigma_g,\tau_1} (1\sigma_g^2) | \hat{a}_{\sigma_u,\tau_2} \hat{a}_{\sigma_u,\tau_1} | 1\sigma_u^2 \rangle$$

$$= (\delta_{\tau_1\alpha}\delta_{\tau_2\beta} - \delta_{\tau_1\beta}\delta_{\tau_2\alpha})^2 \underbrace{\langle vac | vac \rangle}_{1}$$

$$= (\delta_{\tau_1\alpha}\delta_{\tau_2\beta})^2 + (\delta_{\tau_1\beta}\delta_{\tau_2\alpha})^2 = \delta_{\tau_2\bar{\tau}_1}$$ where $\bar{\tau}_1 = \alpha$ if $\tau_1 = \beta$, $\bar{\tau}_1 = \beta$ if $\tau_1 = \alpha$

Conclusion:

$$K = \frac{1}{2} \langle 1\sigma_g 1\sigma_g | 1\sigma_u 1\sigma_u \rangle \underbrace{\sum_{\tau_1\tau_2} \delta_{\tau_2\bar{\tau}_1}}_{\sum_{\tau_1} 1} \Rightarrow \boxed{K = \langle 1\sigma_g 1\sigma_g | 1\sigma_u 1\sigma_u \rangle}$$

or, equivalently, $$K = \int d\vec{r}_1 \int d\vec{r}_2 \frac{\phi_{1\sigma_g}(\vec{r}_1)\phi_{1\sigma_g}(\vec{r}_2)\phi_{1\sigma_u}(\vec{r}_1)\phi_{1\sigma_u}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$\boxed{K = \langle 1\sigma_u 1\sigma_u | 1\sigma_g 1\sigma_g \rangle}$$

(2) $$\phi_{1\sigma_g}(\vec{r}) = \frac{1}{\sqrt{2}}\left(\phi_{1s_A}(\vec{r}) + \phi_{1s_B}(\vec{r})\right)$$

$$\phi_{1\sigma_u}(\vec{r}) = \frac{1}{\sqrt{2}}\left(\phi_{1s_A}(\vec{r}) - \phi_{1s_B}(\vec{r})\right)$$

when $R = d(H_A - H_B) \rightarrow +\infty$, $\phi_{1s_A}(\vec{r})\phi_{1s_B}(\vec{r}) \rightarrow 0$ (no overlap),

therefore $$h_{uu} = \int d\vec{r}\, \phi_{1\sigma_u}(\vec{r}) \left(-\frac{\nabla^2}{2} + v_{ne}(\vec{r})\right)\phi_{1\sigma_u}(\vec{r}) \xrightarrow[R\to+\infty]{} \frac{1}{2}\left(\int d\vec{r}\left[\phi_{1s_A}(\vec{r})\left(-\frac{\nabla^2}{2} + v_{ne}(\vec{r})\right)\phi_{1s_A}(\vec{r})\right] + \int d\vec{r}\left[\phi_{1s_B}(\vec{r})\left(-\frac{\nabla^2}{2} + v_{ne}(\vec{r})\right)\phi_{1s_B}(\vec{r})\right]\right) \xleftarrow[R\to+\infty]{} h_{gg}$$

- Moreover,

$$\langle 1\sigma_u 1\sigma_u | 1\sigma_u 1\sigma_u \rangle = \int d\vec{r}_1 \int d\vec{r}_2 \frac{\phi_{1\sigma_u}(\vec{r}_1)\phi_{1\sigma_u}(\vec{r}_2)\phi_{1\sigma_u}(\vec{r}_1)\phi_{1\sigma_u}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{1}{4}\int d\vec{r}_1 \int d\vec{r}_2 \frac{\left(\phi_{1s_A}(\vec{r}_1) - \phi_{1s_B}(\vec{r}_1)\right)^2\left(\phi_{1s_A}(\vec{r}_2) - \phi_{1s_B}(\vec{r}_2)\right)^2}{|\vec{r}_1 - \vec{r}_2|}$$

thus leading to

$$\langle 1\sigma_u 1\sigma_u | 1\sigma_u 1\sigma_u \rangle \xrightarrow[R\to+\infty]{} \frac{1}{4}\int d\vec{r}_1 \int d\vec{r}_2 \frac{\left[\phi^2_{1s_A}(\vec{r}_1) + \phi^2_{1s_B}(\vec{r}_1)\right]\left[\phi^2_{1s_A}(\vec{r}_2) + \phi^2_{1s_B}(\vec{r}_2)\right]}{|\vec{r}_1 - \vec{r}_2|} \xleftarrow[R\to+\infty]{} \langle 1\sigma_g 1\sigma_g | 1\sigma_g 1\sigma_g \rangle$$

Conclusion: $\boxed{E_u \rightarrow E_g \text{ when } R \rightarrow +\infty}$

- $$K = \frac{1}{4}\int d\vec{r}_1 \int d\vec{r}_2 \frac{\left(\phi_{1s_A}(\vec{r}_1)+\phi_{1s_B}(\vec{r}_1)\right)\left(\phi_{1s_A}(\vec{r}_2)+\phi_{1s_B}(\vec{r}_2)\right)\left(\phi_{1s_A}(\vec{r}_1)-\phi_{1s_B}(\vec{r}_1)\right)\left(\phi_{1s_A}(\vec{r}_2)-\phi_{1s_B}(\vec{r}_2)\right)}{|\vec{r}_1-\vec{r}_2|}$$

$$\xrightarrow[R\to+\infty]{} \frac{1}{4}\int d\vec{r}_1\int d\vec{r}_2 \frac{1}{|\vec{r}_1-\vec{r}_2|}\left(\phi^2_{1s_A}(\vec{r}_1)-\phi^2_{1s_B}(\vec{r}_1)\right)\left(\phi^2_{1s_A}(\vec{r}_2)-\phi^2_{1s_B}(\vec{r}_2)\right)$$

$$= \frac{1}{4}\left(\langle 1s_A 1s_A | 1s_A 1s_A\rangle + \langle 1s_B 1s_B | 1s_B 1s_B\rangle - \underbrace{\int d\vec{r}_1\int d\vec{r}_2 \frac{\phi^2_{1s_A}(\vec{r}_1)\,\phi^2_{1s_B}(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}}_{\to\, 0 \text{ when } R\to+\infty} - \underbrace{\int d\vec{r}_1\int d\vec{r}_2 \frac{\phi^2_{1s_B}(\vec{r}_1)\,\phi^2_{1s_A}(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}}_{\to\, 0 \text{ when } R\to+\infty}\right)$$

Since $\phi_{1s_A}(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_A|}$ and $\phi_{1s_B}(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_B|}$

$$\langle 1s_A 1s_A | 1s_A 1s_A\rangle = \int d\vec{r}_1\int d\vec{r}_2 \frac{e^{-2|\vec{r}_1-\vec{R}_A|}\, e^{-2|\vec{r}_2-\vec{R}_A|}}{\pi^2 |\vec{r}_1-\vec{r}_2|} = \int d\vec{r}_1\int d\vec{r}_2 \frac{e^{-2|\vec{r}_1|}\, e^{-2|\vec{r}_2|}}{\pi^2|\vec{r}_1-\vec{r}_2|} = \langle 1s 1s | 1s 1s\rangle = \langle 1s_B 1s_B | 1s_B 1s_B\rangle$$

Change of variables
$\vec{r}_1 \longrightarrow \vec{r}_1 - \vec{R}_A$
$\vec{r}_2 \longrightarrow \vec{r}_2 - \vec{R}_A$

thus leading to

$$\boxed{K \xrightarrow[R\to+\infty]{} \frac{1}{2}\langle 1s 1s | 1s 1s\rangle}$$

(3) $$[\hat{H}] \xrightarrow[R\to+\infty]{} \begin{bmatrix} E_g & K \\ K & E_g \end{bmatrix}$$ where $K = \frac{\langle 1s 1s | 1s 1s\rangle}{2} > 0$. The ground-state energy is $E_g - K$ (the second energy is $E_g + K$) and the corresponding ground-state wavefunction is $|\Psi_0\rangle = \frac{1}{\sqrt{2}}\left(|1\sigma_g^2\rangle - |1\sigma_u^2\rangle\right) \equiv \begin{bmatrix} 1 \\ -1 \end{bmatrix}\frac{1}{\sqrt{2}}$.

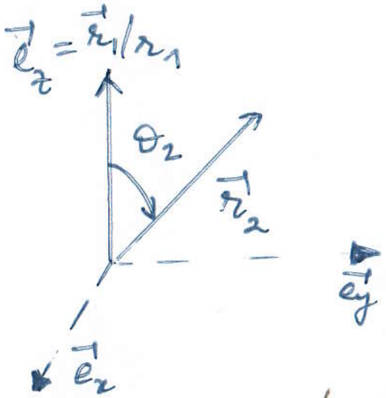
Complement: calculation of the $\langle 1s1s|1s1s\rangle$ integral.

- Let $I_\alpha = \int d\vec{r}_1 \int d\vec{r}_2 \; \frac{1}{\pi^2} \frac{e^{-2\alpha r_1} e^{-2\alpha r_2}}{|\vec{r}_1 - \vec{r}_2|}$.

We note that $I_1 = \langle 1s1s|1s1s\rangle$.

- $I_\alpha = \int d\vec{r}_1 \; \frac{1}{\pi^2} e^{-2\alpha r_1} \left[\int_0^{2\pi} d\varphi_2 \int_0^{\pi} d\theta_2 \int_0^{+\infty} dr_2 \; \frac{r_2^2 \sin\theta_2 \, e^{-2\alpha r_2}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}} \right]$

↓ Choice of spherical coordinates like $\vec{e}_z = \frac{\vec{r}_1}{r_1}$ ← depends on $\vec{r}_1$!



Therefore $I_\alpha = \int d\vec{r}_1 \; \frac{e^{-2\alpha r_1}}{\pi^2} \cdot 2\pi \int_0^{+\infty} dr_2 \; r_2^2 \, e^{-2\alpha r_2} \left[\frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2} \right]_0^{\pi}$

→ $\frac{1}{r_1 r_2} \left(r_1 + r_2 - |r_1 - r_2| \right)$

↓

$\frac{2}{r_1}$ if $r_1 \geq r_2$

$\frac{2}{r_2}$ if $r_1 \leq r_2$

$\Rightarrow I_\alpha = \int d\vec{r}_1 \; \frac{e^{-2\alpha r_1}}{\pi^2} \cdot 4\pi \Bigg(\underbrace{\int_0^{r_1} dr_2 \; \frac{r_2^2 e^{-2\alpha r_2}}{r_1}}_{A_\alpha} + \underbrace{\int_{r_1}^{+\infty} dr_2 \; r_2 e^{-2\alpha r_2}}_{B_\alpha} \Bigg)$

$$A_\alpha = \frac{1}{r_1}\left(\left[\frac{r_2^2\, e^{-2\alpha r_2}}{-2\alpha} \right]_0^{r_1} - \int_0^{r_1} dr_2\; 2r_2 \frac{e^{-2\alpha r_2}}{(-2\alpha)} \right)$$

$$= -\frac{1}{2\alpha r_1} r_1^2 e^{-2\alpha r_1} + \frac{1}{\alpha r_1}\left(\left[r_2 \frac{e^{-2\alpha r_2}}{(-2\alpha)} \right]_0^{r_1} - \int_0^{r_1} dr_2 \frac{e^{-2\alpha r_2}}{(-2\alpha)} \right)$$

$$= \frac{-r_1 e^{-2\alpha r_1}}{(2\alpha)} - \frac{1}{2\alpha^2} e^{-2\alpha r_1} + \frac{1}{\alpha r_1}\left[\frac{1}{2\alpha}\right]\left[\frac{e^{-2\alpha r_2}}{(-2\alpha)} \right]_0^{r_1}$$

$$= \frac{1}{4\alpha^3 r_1} - e^{-2\alpha r_1}\left(\frac{r_1}{2\alpha} + \frac{1}{2\alpha^2} + \frac{1}{4\alpha^3 r_1} \right)$$

and $B_\alpha = \left[r_2 \frac{e^{-2\alpha r_2}}{(-2\alpha)} \right]_{r_1}^{+\infty} - \int_{r_1}^{+\infty} dr_2 \frac{e^{-2\alpha r_2}}{(-2\alpha)} = \frac{r_1 e^{-2\alpha r_1}}{2\alpha} + \frac{1}{2\alpha} \underbrace{\left[\frac{e^{-2\alpha r_2}}{(-2\alpha)} \right]_{r_1}^{+\infty}}_{\frac{1}{2\alpha} e^{-2\alpha r_1}}$

Therefore

$$I_\alpha = \int_0^{2\pi} d\varphi_1 \int_0^{\pi} d\theta_1 \int_0^{+\infty} dr_1\; r_1^2 \sin\theta_1\, e^{-2\alpha r_1} \cdot \frac{\cancel{4}}{\pi} \left[\frac{1}{\cancel{4}\alpha^3 r_1} - \frac{1}{\cancel{4}\alpha^2} e^{-2\alpha r_1} - \frac{e^{-2\alpha r_1}}{\cancel{4}\alpha^3 r_1} \right]$$

$$I_\alpha = 4 \cdot \int_0^{+\infty} dr_1 \left(\frac{r_1}{\alpha^3} e^{-2\alpha r_1} - \frac{r_1^2}{\alpha^2} e^{-4\alpha r_1} - \frac{r_1}{\alpha^3} e^{-4\alpha r_1} \right)$$

$$= 4\left[-\frac{1}{\alpha^3} \underbrace{\int_0^{+\infty} dr_1 \frac{e^{-2\alpha r_1}}{(-2\alpha)}}_{-\frac{1}{2\alpha}\left[e^{-2\alpha r_1}/(-2\alpha)\right]_0^{+\infty}} + \frac{1}{\alpha^2} \int_0^{+\infty} dr_1 (2r_1) \frac{e^{-4\alpha r_1}}{(-4\alpha)} + \frac{1}{\alpha^3} \int_0^{+\infty} dr_1 \frac{e^{-4\alpha r_1}}{(-4\alpha)} \right]$$

$$I_\alpha = 4\left[\frac{1}{4\alpha^5} + \frac{1}{2\alpha^3}\underbrace{\int_0^{+\infty}\frac{e^{-4\alpha r_1}}{(-4\alpha)}dr_1}_{-\frac{1}{4\alpha}\left[e^{-4\alpha r_1}/(-4\alpha)\right]_0^{+\infty}} - \frac{1}{4\alpha^4}\left[\frac{e^{-4\alpha r_1}}{(-4\alpha)}\right]_0^{+\infty}\right]$$

$$I_\alpha = 4\left[\frac{1}{4\alpha^5} - \frac{1}{32\alpha^5} - \frac{1}{16\alpha^5}\right] = \frac{4}{\alpha^5}\times\frac{(8-1-2)}{32}$$

$$\Rightarrow \boxed{I_\alpha = \frac{5}{8\alpha^5}}$$

Conclusion:

$$\boxed{\langle 1s1s|1s1s\rangle = \frac{5}{8}}$$