Kvantumkémia I

Ez egy tételkidolgozás kezdemény. Kis intelligenciával kiegészítve 4-est jó eséllyel el lehet érni vele a vizsgán. Garancia persze nincs.

1/ Variációs elv

Normált hullámfüggvényekre $E = \langle \psi | H | \psi \rangle$, nem normáltakra $E = \dfrac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$ variációja 0, ha $H\psi = E\psi$. Ugyanis:

$$\delta E = \frac{\langle \delta\psi | H | \psi \rangle \langle \psi | \psi \rangle}{\langle \psi | \psi \rangle^2} - \frac{\langle \psi | H | \psi \rangle \langle \delta\psi | \psi \rangle}{\langle \psi | \psi \rangle^2} = 0$$

$$\langle \delta\psi | H | \psi \rangle - E \langle \delta\psi | \psi \rangle = 0$$

$$\langle \delta\psi | H - E | \psi \rangle = 0 \quad \forall \delta\psi \Rightarrow (H - E)\psi = 0 \iff H\psi = E\psi$$

Variációs tétel:

$H\psi_n = E_n \psi_n$ egy $n \in N$, E_n szerint rendezett halmazra. $\#N = M$, $\exists\, E_0$ a legkisebb. Ekkor $\phi = \sum_{i=0}^{k} c_i \psi_i$ állapot ($K \subset N$) E_ϕ energiájára $E_\phi \geq E_0$.

$$E_\phi = \langle \phi | H | \phi \rangle = \sum_{i,k} c_i c_k \overbrace{\langle \psi_i | H | \psi_k \rangle}^{\delta_{ik} E_k} = \sum_i c_i^2 E_i \geq \sum_i c_i^2 E_0 = E_0 \sum_i c_i^2 = E_0$$

Eckart-egyenlőtlenség

Egy alapállapotbeli E_0 energiához közel vagyunk, ha $\dfrac{E_\phi - E_0}{E_0} \ll 1$, de hullámfüggvényben mikor vagyunk elég jók?

$$\eta := \int |\phi - \psi_0|^2 \, d^3x$$

$$\langle \phi - \psi_0 | \phi - \psi_0 \rangle = \underbrace{\langle \phi | \phi \rangle}_{1} + \underbrace{\langle \psi_0 | \psi_0 \rangle}_{1} - 2\langle \phi | \psi_0 \rangle = 2 - 2c_0 = \eta$$

$$c_0 = 1 - \eta/2 \qquad c_0^2 = 1 - \eta + \eta^2/4 \approx 1 - \eta \quad \Rightarrow \quad \eta \approx 1 - c_0^2$$

$$E_\phi - E_0 = \sum_n c_n^2 E_n - \sum_n c_n^2 E_0 = \sum_{n=1}^{M} c_n^2 (E_n - E_0) \geq \sum_{n=1}^{M} c_n^2 (E_1 - E_0) = (1 - c_0^2)(E_1 - E_0)$$

$$\frac{E_\phi - E_0}{E_1 - E_0} \geq 1 - c_0^2 \approx \eta$$

Momentumok módszere

Egy ψ sajátfüggvénye $(H-E)|\psi\rangle = 0$, egy nem sajátfüggvényre $H-E|\phi(a_1, a_2, \dots a_N)\rangle \neq 0$

Az $a_1, a_2, \dots, a_N$ paramétereket jól lenne megválasztani, hogy az érték minimális legyen. Ennél egyszerűbb, ha $\langle f_\mu | H-E | \phi\rangle := m_\mu$ (súlyfüggvény; momentum), $\sum_\mu m_\mu^2$ értékét akarjuk minimalizálni.

$$F := \sum_{\mu=1}^{M} \left| \langle f_\mu | H-E | \phi(a_1, a_2, \dots, a_N)\rangle \right|^2$$

$$\frac{\partial F}{\partial a_i} \overset{!}{=} 0 \quad \forall i \in \{1, \dots, N\}$$

és

$$\frac{\partial F}{\partial E} \overset{!}{=} 0$$

$N+1$ feltétel. Ha $M \leq N+1$, akkor elérhető, hogy mindegyik momentum 0 legyen.

Ezzel más helyeken optimalizáljuk a hullámfüggvényt, mintha $\frac{\partial}{\partial a_i} \langle \phi | H-E | \phi \rangle \overset{!}{=} 0$ tekintenénk.

f generátorfüggvény, ha $\frac{\partial}{\partial b_\mu} f(b_1, b_2, \dots, b_M) = f_\mu$

$\boxed{\text{2/Perturbációszámítás}}$ Rayleigh-Schrödinger

$H = H^{(0)} + W$ $\quad H^{(0)} \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}$ megoldásokat ismerjük

$H^{\lambda} = H^{(0)} + \lambda W$ $\quad H \Psi_a = E_a \Psi_a$ megoldásokat keressük

ha $\lambda = 1$, akkor $H^{\lambda} = H$, ha 0, akkor $H^{\lambda} = H^{(0)}$

$$E_a = \sum_{\mu} \lambda^{\mu} E_a^{(\mu)}$$

$$\Psi_a = \sum_{\mu} \lambda^{\mu} \Psi_a^{(\mu)} \quad \text{ahol} \quad \langle \Psi_a | \Psi_a^{(0)} \rangle \overset{!}{=} 1 \quad \Rightarrow \langle \Psi_a^{(i)} | \Psi_a^{(0)} \rangle = \delta_{i0}$$

$$H^{\lambda} \Psi_a = E_a \Psi_a \quad \Leftrightarrow \quad \sum_{\mu} \lambda^{\mu} H^{(0)} \Psi_a^{(\mu)} + \sum_{\mu} \lambda^{\mu+1} W \Psi_a^{(\mu)} = \sum_{\mu} \lambda^{\mu} E_a^{(\mu)} \sum_{\nu} \lambda^{\nu} \Psi_a^{\nu}$$

$$H^{(0)} \Psi_a^{(\mu)} + W \Psi_a^{(\mu-1)} = \sum_{\nu} E_a^{(\nu)} \Psi_a^{(\mu-\nu)} \quad / \cdot \langle \Psi_a^{(0)} |$$

$$\overbrace{\langle \Psi_a^{(0)} | H^{0} | \Psi_a^{(\mu)} \rangle}^{E_a^{(0)} \langle \Psi_a^{(0)} | \Psi_a^{\mu} \rangle = 0} + \langle \Psi_a^{(0)} | W | \Psi_a^{(\mu-1)} \rangle = E_a^{(\mu)}$$

$\Psi_a^{(\mu)} = \sum_i c_{ia} \Psi_i^{(0)}$ sorfejtést beírva, $W_{ia} := \langle \Psi_i^{(0)} | W | \Psi_a^{(0)} \rangle$

$$E_a^{(1)} = - \frac{W_{a0}}{E_a^{(0)} - E_0^{(0)}} \qquad E_a^{(2)} = - \sum_{i \neq a} \frac{|W_{ai}|^2}{E_i^{(0)} - E_a^{(0)}}$$

$\boxed{\text{Brillouin-Wignerrel}}$ az energiát nem fejtjük sorba, $E_a^{(2)} = - \sum_{i \neq a} \frac{|W_{ai}|^2}{E_i^{(0)} - E}$

Nem extenzív, de kvázidegenerált esetben jobb, mint a RS.

$\boxed{\text{RS extenzív}}$ ugyanis $H = H_a + H_b = H_a^{(0)} + W_a + H_b^{(0)} + W_b := H^{(0)} + W$

$$H_A^{(0)} \Psi_{A,a}^{(0)} = E_{A,a}^{(0)} \Psi_{A,a}^{(0)}$$

$$H_B^{(0)} \Psi_{B,b}^{(0)} = E_{B,b}^{(0)} \Psi_{B,b}^{(0)}$$

$$E_0^{(2)} = - \sum_{i \neq 0} \frac{|W_{0i}|^2}{E_i^{(0)} - E_0^{(0)}} = - \sum_{i \neq 0} \frac{|\langle \Psi_{A0}^{(0)} \Psi_{B0}^{(0)} | W_A + W_B | \Psi_{A0}^{(0)} \Psi_{B,i}^{(0)} \rangle|^2}{\left(E_{A,0}^{(0)} + E_{B,i}^{(0)}\right) - \left(E_{A,0}^{(0)} + E_{B,0}^{(0)}\right)}$$

$$- \sum_{i \neq 0} \frac{|\langle \Psi_{A0}^{(0)} \Psi_{B,0}^{(0)} | W_A + W_B | \Psi_{A,i}^{(0)} \Psi_{B,0}^{(0)} \rangle|^2}{\left(E_{A,i}^{(0)} + E_{B,0}^{(0)}\right) - \left(E_{A,0}^{(0)} + E_{B,0}^{(0)}\right)} = E_{B,0}^{(2)} + E_{A,0}^{(2)}$$

Redukált rezolvens

$$Q := -\sum_{k\neq 0} \frac{|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|}{E_k^{(0)}-E_0^{(0)}} \Rightarrow E_0^{(2)} = \langle \psi_0^{(0)} | W Q W | \psi_0^{(0)} \rangle$$

$$(H^{(0)}+W)\,\psi = (E_0^{(0)}+\Delta E)\,\psi$$

$$(H^{(0)}-E_0^{(0)})\,\psi = (\Delta E - W)\,\psi$$

$$\underbrace{Q\left(H^{(0)}-E_0^{(0)}\right)}_{P}\psi = Q(\Delta E - W)\,\psi$$

$$P\left(H^{(0)}-E_0^{(0)}\right)^{-1} = \left(1-|0\rangle\langle 0|\right)\sum_{i=0}^{\infty}\frac{|i\rangle\langle i|}{E_i^{(0)}-E_0^{(0)}} = \sum_{i=0}^{\infty}\frac{|i\rangle\langle i|}{E_i^{(0)}-E_0^{(0)}} - \frac{|0\rangle\langle 0|}{E_0^{(0)}-E_0^{(0)}} =$$

$$= \sum_{i\neq 0}^{\infty}\frac{|i\rangle\langle i|}{E_i^{(0)}-E^{(0)}} = -Q$$

$$\psi - |0\rangle\overbrace{\langle 0|\psi_0\rangle}^{1} = Q(\Delta E - W)\,\psi$$

$$\psi = \underset{\displaystyle |0\rangle}{\underset{\shortparallel}{\psi_0^{(0)}}} + Q(\Delta E - W)\,\psi$$

3/ Partícionálási eljárás

P, O projektorok, $\quad P+O=I, \quad P^2=P, \quad O^2=O, \quad PO=OP=\emptyset$

$$H\Psi = E\Psi$$

$$H(P+O)\Psi = E(P+O)\Psi \qquad \Big/ \cdot O, \ \cdot P$$

$$(OHP + OHO)\Psi = EO\Psi$$

$$(PHP + PHO)\Psi = EP\Psi \quad \Rightarrow \quad (PH - E)P\Psi = -PHO\Psi$$

$$P\Psi = -(PH-E)^{-1}PHO\Psi$$

$$OHO\Psi - OH(PH-E)^{-1}PHO\Psi = E\overbrace{O\Psi}^{:=\phi}$$

$$\Big/ \ O = O^2$$

$$\underbrace{\left[OH\left(1-(PH-E)^{-1}PH\right)O\right]}_{H_{eff}}\phi = E\phi$$

H_{eff}, sajátfüggvénye az O terében van.

$$T = P\left(\eta O + P(E-H)P\right)^{-1}P$$

1) $P(E-H)T = P$, ugyanis

$$\left(\eta O + P(E-H)P\right)\left(\eta O + P(E-H)P\right)^{-1} = 1 \qquad \Big/ \ P \bullet P$$

$$P(E-H)P\underbrace{\left(\eta O + P(E-H)P\right)^{-1}P}_{T} = P$$

2) $OT = TO = \emptyset$

$\Omega := O + THO \quad \boxed{\text{Hullámoperátor}}$

$$P(H-E)O + \overbrace{P(H-E)T}^{-P}HO = PHO - PHO - \overbrace{PEO}^{\emptyset} = 0$$

$$(H-E)\Omega = (O+P)(H-E)\Omega = O(H-E)\Omega + \overbrace{P(H-E)\Omega} = O(H-E)(O+THO) =$$

$$= O(H-E)O + \overbrace{O(H-E)THO}^{OHTHO} = O(H-E+HTH)O \qquad OEO \overset{!}{=} O(H+HTH)O$$

$$OET = \emptyset$$

Ekkor $(H-E)\Omega = 0$

$$H\Omega = E\Omega$$

Ekkor $\Psi = \Omega\varphi$-re $\quad \boxed{H\Psi = H\Omega\varphi = E\Omega\varphi = E\Psi}$

$$O \doteq |\varphi\rangle\langle\varphi| \quad \text{és} \quad P = 1 - O$$

$$|\varphi\rangle\langle\varphi|E|\varphi\rangle\langle\varphi| = |\varphi\rangle\langle\varphi| H + HTH |\varphi\rangle\langle\varphi| \qquad / \cdot \langle\varphi| \,.\, |\varphi\rangle$$

$$E = \langle\varphi| H + HTH |\varphi\rangle \qquad \text{Ha} \quad \varphi = \varphi_0^{(0)}, \quad H = H^{(0)} + W$$

$$E = \langle\varphi_0^{(0)}| H_0 + W | \varphi_0^{(0)}\rangle + \underbrace{\langle\varphi_0^{(0)}| HTH |\varphi_0^{(0)}\rangle} = \langle\varphi_0^{(0)}| H^{(0)} |\varphi_0^{(0)}\rangle +$$

$$+ \langle\varphi_0^{(0)}| \underbrace{W + WTW} |\varphi_0^{(0)}\rangle$$

$$\langle\varphi_0^{(0)}| \underbrace{H^{(0)}} TH|0\rangle$$

$$E_0^{(0)} \langle\varphi_0^{(0)}| TH|0\rangle \sim \langle\varphi_0^{(0)}| P \ldots |0\rangle = 0 \qquad := t$$

$$E = \langle H^{(0)}\rangle + \langle t\rangle \qquad t = W + WTW$$

$TP = T$, ezért jobbról megszorozhatunk P-vel

$$T = \frac{P}{E-H} = \frac{P}{\underbrace{E - H^{(0)}}_{A} - \underbrace{W}_{B}} = P \cdot \frac{1}{E - H^{(0)}} + P\frac{1}{E-H^0} W P \frac{1}{E-H^0} + P\frac{1}{E-H^0} W P \frac{1}{1-H^0} W P \frac{1}{1-H^0} + \ldots$$

$$(A-B)^{-1} = A^{-1} + (A-B)^{-1} B A^{-1} = A^{-1} + A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} + \ldots$$

$$T = P\frac{1}{E-H^{(0)}} + P\frac{1}{E-H^0} WT := Q + QWT$$

$$\left[t = W + W(Q + QWT)W = W + WQW + WQWTW = W + WQ(W + WTW) = \right.$$

$$= \boxed{W + WQt} \qquad \text{Lippmann–Sch.}$$

$$H\Psi_i = E_i \Psi_i \implies E_i \Psi_i - H^{(0)} \Psi_i = W \Psi_i \qquad \phi_i = O \Psi_i, \quad \Omega \phi_i = \Psi_i$$

$$(1) \qquad E_i \Psi_i - H^{(0)} \Omega \phi_i = W \Omega \phi_i \qquad / \cdot \Omega O$$

$$-\ (2) \qquad E_i \Psi_i - \Omega H^{(0)} \phi_i = \Omega O W \Omega \phi_i$$

$$[\Omega, H^0]\, O \Psi_i = (1 - \Omega O) W \Omega O \Psi_i \qquad \forall i$$

$$\boxed{[\Omega, H^0]\, O = (1 - \Omega O) W \Omega O} \qquad \text{Bloch - egyenlet}$$

4 Másod kvantált formalizmus

$\boxed{\text{Wick-tétel}}$

$$\langle vac | a_\mu^+ a_\nu | vac \rangle = 0$$

$$\langle vac | a_\nu a_\mu^+ | vac \rangle = \delta_{\nu\mu}$$

$$\langle \varrho | a_\nu^+ a_\mu | \varrho \rangle = \langle vac | a_\varrho a_\nu^+ a_\mu a_\varrho^+ | vac \rangle = \delta_{\varrho\nu} \delta_{\mu\varrho}$$

$$\langle \varrho | a_\nu a_\mu^+ | \tau \rangle = \langle vac | a_\varrho a_\nu a_\mu^+ a_\tau^+ | vac \rangle = \delta_{\varrho\tau} \delta_{\nu\mu} - \delta_{\varrho\mu} \delta_{\nu\tau}$$

Általánosan $\langle vac | a_1 a_2 a_3^+ a_4^+ | vac \rangle = \delta_{23} \delta_{14} - \delta_{24} \delta_{13}$

$\boxed{\text{Fermi-vákuum}}$ $\boxed{\text{Elektron-lyuk szimmetria}}$

$$\langle HF | a_\mu^+ a_\nu | HF \rangle = \delta_{\mu\nu} \qquad \langle HF | a_\nu a_\mu^+ | HF \rangle = 0$$

$$b_i^+ = \begin{cases} a_i & \text{ha } i \text{ occ.} \\ a_i^+ & \text{ha } i \text{ virt} \end{cases} \qquad b_i = \begin{cases} a_i^+ & \text{ha } i \text{ occ} \\ a_i & \text{ha } i \text{ virt} \end{cases}$$

Ezek a b_i, b_i^+ -ek u.a. teszik, mint a_i, a_i^+, csak a HF állapotokon.

$A = \sum_{\mu\nu} A_{\mu\nu} a_\mu^+ a_\nu$ A egyrészecske-operátor

$$\langle A \rangle = \sum_{\mu\nu} A_{\mu\nu} \langle a_\mu^+ a_\nu \rangle := \sum_{\mu\nu} A_{\mu\nu} P_{\nu\mu} = \mathrm{Tr}(\underline{\underline{A}} \cdot \underline{\underline{P}})$$

$P_{\nu\mu} = \langle \Psi | a_\mu^+ a_\nu | \Psi \rangle$ Ha $\Psi = HF$, μ-k pedig a m.o.-k, P diagonális

Ha $\Psi \neq HF$, P nem diagonális, de unitér trafóval azzá tehető. Az így nyert pályák a MO-k lin. komb, ún. term. pályák.

$B = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] a_\mu^+ a_\nu^+ a_\sigma a_\lambda$

analóg $B_{\mu\nu\lambda\sigma}$

$[\mu\nu|\lambda\sigma] = \int dx_1 \int dx_2 \, \varphi_\mu(1) \varphi_\nu(2) B \varphi_\lambda(1) \varphi_\sigma(2)$

$$\langle B \rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \underbrace{\langle \Psi | a_\mu^+ a_\nu^+ a_\sigma a_\lambda | \Psi \rangle}_{:= \Gamma_{\lambda\sigma\mu\nu}} := \frac{1}{2} \sum_{\substack{\mu\nu \\ \lambda\sigma}} [\mu\nu|\lambda\sigma] \Gamma_{\lambda\sigma\mu\nu} = \frac{1}{2} \mathrm{Tr}(\underline{\underline{A}} \, \underline{\underline{\Gamma}})$$

Ebben $M^{HF}_{\lambda\sigma\mu\nu} = \langle HF | \mu^+ \nu^+ \sigma \lambda | HF \rangle = P_{\mu\lambda} P_{\nu\sigma} - P_{\mu\sigma} P_{\nu\lambda}$ AO és MO-ban is

Spinpályák figyelembe-vétele

$$\begin{matrix} \mu & \nu & \lambda & \sigma \\ \updownarrow & \updownarrow & \updownarrow & \updownarrow \\ \binom{m}{\sigma_m} & \binom{n}{\sigma_n} & \binom{\ell}{\sigma_\ell} & \binom{s}{\sigma_s} \end{matrix}$$

$$\langle A \rangle = \sum_{\mu\nu} A_{\mu\nu} P_{\nu\mu} = \sum_{\substack{mn \\ \sigma_m \sigma_n}} A^{\sigma_m \sigma_n}_{mn} P^{\sigma_m \sigma_n}_{\nu\mu}$$

$\downarrow =$

ha A spinfüggetlen

$$\langle A \rangle = \sum_{\substack{m,n \\ \sigma}} A_{mn} P^{\sigma}_{mn} \qquad \left\langle \begin{matrix}\sigma_m \\ m\end{matrix} \middle| A \middle| \begin{matrix}\sigma_n \\ n\end{matrix} \right\rangle \stackrel{\downarrow}{=} A_{mn} \delta_{\sigma_m \sigma_n}$$

$$\langle A \rangle := \sum_{m,n} A_{mn} P_{mn} \qquad \text{vagyis} \quad P^\alpha + P^\beta = P$$

$$P^\alpha - P^\beta := R$$

térbeli pályákkal

$$E = \sum_{\mu\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \left(P_{\mu\lambda} P_{\nu\sigma} - P_{\mu\sigma} P_{\nu\lambda} \right)$$

$$= \sum_{m,n} h_{mn} P_{nm} + \frac{1}{2} \sum_{\substack{mn\ell s \\ \sigma_m \sigma_n \\ \sigma_\ell \sigma_s}} \underbrace{\left[\begin{matrix}\sigma_m & \sigma_n \\ m & n\end{matrix} \middle| \begin{matrix}\sigma_\ell & \sigma_s \\ \ell & s\end{matrix} \right]}_{\sim \delta_{\sigma_m \sigma_\ell} \delta_{\sigma_n \sigma_s}} \left(P^{\sigma_m \sigma_\ell}_{m\ell} P^{\sigma_n \sigma_s}_{ns} - P^{\sigma_m \sigma_s}_{ms} P^{\sigma_n \sigma_\ell}_{n\ell} \right)$$

$$= \mathrm{Tr}(\underline{\underline{h}}\, \underline{\underline{P}}) + \frac{1}{2} \sum_{mn\ell s} [mn|\ell s] \left[P_{m\ell} P_{ns} - \underbrace{\sum_\sigma P^\sigma_{ms} P^\sigma_{n\ell}}_{P^{\alpha\alpha}_{ms} P^{\alpha\alpha}_{n\ell} + P^{\beta\beta}_{ms} P^{\beta\beta}_{n\ell}} \right]$$

zárt héj esetén

$R = 0, \quad \frac{P}{2} = P^\alpha$

$$= \mathrm{Tr}(\underline{\underline{h}}\, \underline{\underline{P}}) + \frac{1}{2} \sum_{mn\ell s} [mn|\ell s] \left[P_{m\ell} P_{ns} - \frac{1}{2} P_{ms} P_{n\ell} \right] = \mathrm{Tr}(\underline{\underline{h}}\, \underline{\underline{P}}) + \frac{1}{2} \sum_{\substack{mn \\ \ell s}} P_{m\ell} P_{ns} \left([mn|\ell s] - \frac{[mn|s\ell]}{2} \right)$$

$$E = \langle H \rangle = \sum_{\mu\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\substack{\mu\nu \\ \lambda\sigma}} P_{\mu\lambda} P_{\nu\sigma} \left([\mu\nu|\lambda\sigma] - [\mu\nu|\sigma\lambda] \right)$$

$\sigma \to \mu \to \sigma$

$$= \frac{1}{2} \sum_{\mu\nu} \left[h_{\mu\nu} + \underbrace{\left(h_{\mu\nu} + \sum_{\lambda\sigma} \left([\sigma\nu|\lambda\mu] - [\sigma\nu|\mu\lambda] \right) P_{\sigma\lambda} \right)}_{F_{\mu\nu}} \right] P_{\nu\mu}$$

$$= \frac{1}{2} \mathrm{Tr}\left[(\underline{\underline{h}} + \underline{\underline{F}}) \underline{\underline{P}} \right]$$