Matice hustoty

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Vnitřní součin [inner product]:

$$\langle \Phi | \Psi \rangle = \sum_i \Phi_i^* \Psi_i \qquad \int \Phi^*(r) \Psi(r) \, dr$$

In some basis $\Psi_i \Phi_i$ continuous

báze např. vl. stavy $\hat{\mathrm{H}} : f_i$

$$\langle f_i | f_j \rangle = \delta_{ij}$$

$$|\Psi\rangle = \sum_i \Psi_i | f_i \rangle$$

spojité spektrum:

$$|\Psi\rangle = \int \Psi(r) | r \rangle \, dr \qquad \langle r | r' \rangle = \delta(r - r')$$

$$\Psi(r) = \langle r | \Psi \rangle$$

Projekční op:

$$\widehat{P}_x = |x\rangle\langle x|$$

$$P_i|\Psi\rangle = |f_i\rangle\langle f_i|\Psi\rangle$$

Idempotentní op:

$$\widehat{P}_x.\widehat{P}_x = \widehat{P}_x$$

$$|\Psi\rangle = \sum_i \langle f_i|\Psi\rangle| f_i\rangle = \left\{\sum_i | f_i\rangle\langle f_i|\right\}|\Psi\rangle$$

$$\sum_i P_i = \hat{1}$$

"closure relatio"

spoj. op:

$$\int |r\rangle\langle r|dr = \int dr\widehat{P}_r = \hat{1}$$

$$\langle f_i|\widehat{A}|\Psi\rangle = \sum_j \langle f_i|\widehat{A}| f_j\rangle\langle f_j|\Psi\rangle = \langle f_i|\Psi'\rangle$$

$$\widehat{A}|\Psi\rangle = |\Psi'\rangle$$

s.s.:

$$\langle r'|\widehat{A}|\Psi\rangle = \int drA_{(r',r)}\Psi_{(r)} = \Psi_{(r')}$$

$$A_{(r',r)} = \langle r'|\widehat{A}|r\rangle$$

Platí-li $\widehat{A}_{(r',r)} = A_{(r)}\delta_{(r'-r)}$ je op $\widehat{A}$ lokální

N částicový system

prostory:

$$\kappa_{\mathrm{N}}^{\mathrm{A}}, \kappa_{\mathrm{N}}^{S} : \left|\alpha_1 a_2 \ldots a_N\right\rangle = \left|\alpha_1\right\rangle \left|\alpha_2\right\rangle \ldots \left|\alpha_N\right\rangle$$

$$\kappa_{\mathrm{N}}^{\mathrm{A}} : \left|\alpha_1 a_2 \ldots a_N\right\rangle = \frac{1}{\sqrt{N!}} \sum^{P} (-1)^P \left|\alpha_1 a_2 \ldots a_N\right\rangle$$

kde

$$\sum_{P:\alpha_1 \ldots a_N} \left|\alpha_1 \ldots a_N\right\rangle \left\langle \alpha_1 \ldots a_N\right| = \hat{1}$$

a též:

$$\sum_{\alpha_1 \ldots a_N} \frac{1}{N!} \left| \quad \right\rangle \left\langle \quad \right| = \hat{1}$$

v prostoru N částic

Operátory hustoty

Obecný stav N částic:

$$\Psi_N(x_1 \dots x_N)\Psi^*_N(x_1 \dots x_N) \sim pp.$$

$$\gamma_N(x_1', x_2' \dots x_N', x_1, x_2 \dots x_N) = \Psi_N \Psi_N^* \equiv \hat{\gamma}_N = \left|\Psi_N\right\rangle\left\langle\Psi_N\right|$$

$$(x_1' \dots x_N' \,|\, \hat{\gamma}_N \,|\, x_1 \dots x_N) = (x_1' \dots x_N' \left|\Psi\right\rangle\left\langle\Psi^*\right| x_1 \dots x_N)$$

$$\Psi(x_1' \dots x_N') \qquad \Psi^*(x_1 \dots x_N)$$

$$tr(\hat{\gamma}_N) = \int \Psi_N(x^N)\Psi_N^*(x^{N(')})\, dx^N = 1 \quad x^N = x^{N'}$$

Pak $\forall \hat{A}$:

$$\left\langle \hat{A} \right\rangle = tr(\hat{\gamma}_N \hat{A}) = tr(\hat{A}\hat{\gamma}_N)$$

Př.: Dokažte

Ψ i γ mají stejnou informaci

Ψ má fázový faktor (lib), $\hat{\gamma}$ ne! γ je Hermitovská

$\langle \hat{A} \rangle$...i pro systémy, které nejsou superpozicí stavů Ψ a $\hat{H}$

(Ψ_x je podprostor $\hat{\kappa}_N$)

Ψ...čistý stav

γ...i smíšený => $\Gamma = \sum_i p_i \left| \Psi_i \right\rangle \left\langle \Psi_i \right|$ Γ je Hermitovská

$$p_i \geq 0 \qquad \sum_i p_i = 1$$

čistý stav $\exists ! \, p_i = 1$

$$\left\langle f_k \right| \hat{\Gamma} \left| f_l \right\rangle = \sum_i p_i \left\langle f_k | \Psi_i \right\rangle \left\langle \Psi_i | f_l \right\rangle = \sum_i p_i (\left\langle f_l | \Psi_i \right\rangle \left\langle \Psi_i | f_k \right\rangle)^*$$

$$= \left\langle f_l \right| \hat{\Gamma} \left| f_k \right\rangle^*$$

$$\langle f_k | \hat{\Gamma} | f_k \rangle = \sum_i p_i \left| \langle f_k | \Psi_i \rangle \right|^2 \quad \geq 0$$

ALE

$$\hat{\gamma}_N \hat{\gamma}_N = |\Psi\rangle\langle\Psi|\Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi| = \hat{\gamma}_N$$

nic méně

$$\hat{\Gamma}\hat{\Gamma} = \sum_i p_i^2 |\Psi_i\rangle\langle\Psi_i| \neq \hat{\Gamma}!! \qquad \langle\hat{A}\rangle = tr(\hat{\Gamma}\hat{A}) = \sum_i p_i \langle\Psi_i|A|\Psi_i\rangle$$

platí i pro $\hat{H}$

$$i\hbar\frac{\partial}{\partial t}|\Psi_N\rangle = \hat{H}|\Psi_N\rangle$$

!!!!

$$\frac{\partial}{\partial t}(\gamma_N) = (\frac{\partial}{\partial t}|\Psi\rangle)\langle\Psi| + |\Psi_N| \frac{\partial}{\partial t}|\Psi\rangle = \frac{H}{i\hbar}|\Psi\rangle\langle\Psi| - |\Psi\rangle\langle\Psi|\frac{H}{i\hbar}$$

$$i\hbar\frac{\partial}{\partial t}\hat{\Gamma} = \left[\hat{H},\hat{\Gamma}\right] \qquad \left[\hat{H},\hat{\Gamma}\right] = 0$$

stacionární stav => stejné vektory

Redukovaná matice hustoty (bezspinová)

$$H = h(1) + g(1,2)$$ => ?lze $\Psi_N \Psi_N^*$ zredukovat např. $\int dx_3 \dots dx_N$

Koncept RDM:

$$\gamma_p(x_1', \dots x_p', x_1 x_2 \dots x_p) = \binom{N}{p} \int \dots \int \gamma_N(x_1', \dots x_N, x_1 x_2 \dots x_N) dx_{p+1} \dots dx_N$$

a spec:

$$\gamma_2(x_1' x_2', x_1 x_2) = \frac{N(N-1)}{2} \int \dots \int \Psi(x_1' \dots x_N) \Psi^*(x_1 \dots x_N) dx_3 \dots dx_N$$

s normou: počet el. párů

$$tr\gamma_2(x_1' x_2', x_1 x_2) = \iint \gamma_2(x_1 x_2, x_1 x_2) dx_1 dx_2 = \frac{N(N-1)}{2}$$

a

$$\gamma_1(x_1', x_1) = N \int \dots \int \Psi(x_1' x_2 \dots x_N) \Psi^*(x_1 x_2 \dots x_N) dx_2 \dots dx_N$$

$$tr\gamma_1(x_1', x_1) = \int \gamma(x_1, x_1) dx_1 = N$$

$\gamma_1, \gamma_2, \ldots$ jsou prostor. reprezentace $\hat{\gamma}_1, \hat{\gamma}_2, \ldots$ v 1- a 2- částicovém Herm. prostoru

$\gamma_i(\ ) \geq 0$ a $\gamma_{\substack{1\\2}}(x_1', x_1) = \gamma_{\substack{1\\2}}^*(x_1, x_1')$

$$\gamma_2(x_1'x_2', x_1 x_2) = -\gamma_2(x_2'x_1', x_1 x_2) = -\gamma_2(x_1'x_2', x_2 x_1) = \gamma_2(x_2'x_1', x_2 x_1)$$

Hermitovský operator $\hat{\gamma}_i$ => $\exists!$ vlastní vektory a čísla:

$$\int \gamma_1(x_1', x_1)\Psi_i(x_1)dx_1 = \mu_i \Psi_i(x_1')$$

přirozené orbitaly a obsazovací čísla

$$\int \gamma_2(x_1'x_2', x_1 x_2)\Theta_i(x_1 x_2)dx_1\, dx_2 = g_i \Theta_i(x_1'x_2')$$

net. Geminály

$$\hat{\gamma}_1 = \sum_i \mu_i |\Psi_i\rangle\langle\Psi_i| \qquad \gamma_1(x_1', x_1) = \sum_i \mu_i \Psi_i(x_1')\Psi_i^*(x_1)$$

$$\hat{\gamma}_2 = \sum_i \mu_i |\Theta_i\rangle\langle\Theta_i| \qquad \mu_i \geq 0 \quad g_i \geq 0$$

g_i

Smíšené stavy

$$\Gamma_p(x_1',\dots x_p', x_1 x_2 \dots x_p) = \binom{N}{p} \int \dots \int \Gamma_N(x_1',\dots x_p' x_{p+1} \dots x_N, x_1 x_2 \dots x_N) dx_{p+1} \dots dx_N$$

$$\Gamma_1(x_1', x_1) = N \int \dots \int \sum_i p_i \Psi_i(x_1' x_2 \dots x_N) \Psi^*(x_1 x_2 \dots x_N) dx_2 \dots dx_N$$

$$\Psi_N; \hat{O}_1 = \sum_i^N O_1(x_i, x_i') \qquad \langle O_1 \rangle = tr(O_1 \gamma_N) = \int O_1(x_1, x_1') \gamma_1(x_1', x_1) dx_1' dx_1$$

O_1 je lokální $\Leftrightarrow$ $\hat{O}_1 = \sum_i O_1(x_i)$

Př.: $\hat{O}_2 = \sum_{i<j}^N O_2(x_i x_j)$ $\qquad \hat{J}$, ne $\hat{K}$!

$$\langle \hat{O}_2 \rangle = ? \qquad E = tr(\hat{H} \hat{\gamma}_N) = E[\gamma_1 \gamma_2] = E[\gamma_2] = ?$$

γ_k (v 1. iteraci) musí odpovídat nějaké antisym. Ψ !

∀odhady (1. iterace) už musí 6-dim. fce ≈ “ Ψ “

N-reprezentabilita

Jednodušší je hledat Γ_2 (ve smíšených stavech, kde není Ψ ale ρ)

...“ensemble N-reprezentability“

$$E_0 = tr(\hat{\mathrm{H}}\hat{\Gamma}^{\circ}_N) \leq tr(\hat{\mathrm{H}}\hat{\Gamma}_N)$$

$$\hat{\Gamma}^{\circ}_N \approx> \gamma_N \quad \text{(není-li zákl. stav degenerován)}$$

Matice hustoty (bezspinová)

$$\rho_1(r_1', r_1) = \int \gamma_1(r_1' s_1^{(')}, r_1 s_1)ds_1 =$$

$$= N\int \ldots \int \Psi(r_1' s_1 x_2 \ldots x_N)\Psi^*(r_1 s_1 x_2 \ldots x_N)ds_1 dx_2 \ldots dx_N$$

$$s_1' = s_1$$

Př.: napiš:

$$\rho_2(r_1' r_2', r_1 r_2) =$$

diagonální elementy ρ_2 lze zapsat:

$$\rho_2(r_1 r_2) = \rho_2(r_1 r_2, r_1 r_2) = \frac{N(N-1)}{2}\int \ldots \int |\Psi|^2 ds_1 ds_2 dx_3 \ldots dx_N$$

$$\rho_1(r_1) = \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots = N.\int - \| -$$

$$\rho_1(r_1', r_1) = \frac{2}{N-1}\int \rho_2(r_1' r_2', r_1 r_2)dr_2$$

$$\hat{O}_1, \hat{O}_2 = ...$$

$$E = E[\rho_1(r_1', r_1)\rho_2(r_1 r_2)] = E[\rho_2(r_1' r_2', r_1 r_2)] =$$

$$= \int [-\frac{1}{2}\nabla_{r_1}^2 \rho_1(r_1', r_1)]_{r_1' = r_1} dr_1 + \int v(r_1)\rho(r)dr + \iint \frac{1}{r_{12}}\rho(r_1 r_2)dr_1 dr_2$$

$$!\,\mathrm{J}[\rho] = \frac{1}{2}\iint \frac{1}{r_{12}}\rho_1(r_1)\rho_1(r_2)dr_1 dr_2\,!$$

$$\rho_2(r_1 r_2) = \frac{1}{2}\rho(r_1)\rho(r_2).[1 + h(r_1 r_2)]$$ párová korelační fce

$$\frac{N-1}{2}\rho(r_1) = \frac{1}{2}\rho(r_1).[N + \int \rho(r_2)h(r_1 r_2)dr_2]$$

!!

a tudiž:

$$\int \rho(r_2)h(r_1r_2)dr_2 = -1 \qquad \overset{r_1}{\forall R_1}$$

Slater: výměnné-korelační díra

$$\rho_{xc}(r_1r_2) = \rho(r_2)h(r_1r_2)$$

$$\int \rho_{xc}(r_1r_2)dr_2 = -1$$

$$V_{ee} = \iint \frac{1}{r_{12}}\rho(r_1r_2)dr_1dr_2 = \mathrm{J}[\rho] + \frac{1}{2}\iint \frac{1}{r_{12}}\rho_1(r_1)\rho_{xc}(r_1r_2)dr_1dr_2$$

$$\rho_1(r_1', r_1) = \rho_1^{\alpha\alpha}(r_1', r_1) + \rho_1^{\beta\beta}(r_1', r_1)$$

$$\rho(r) = \rho^{\alpha}(r) + \rho^{\beta}(r) \qquad \rho^{\sigma}(r) = \rho_1^{\sigma\sigma}(r', r) \qquad r_1' = r_1$$

Spinová hustota:

$$\vartheta = \rho^{\alpha}(r) - \rho^{\beta}(r)$$

$$\rho_2(r_1' r_2', r_1 r_2) = \rho_2^{\alpha\alpha}(\ldots) + \rho_2^{\beta\beta}(\ldots) + \rho_2^{\alpha\beta}(\ldots) + \rho_2^{\beta\alpha}(\ldots)$$

1.řád RDM: Fock-Dirac DM:

$$\gamma_1(x_1' x_1) = \sum_i \Psi_i(x_1') \Psi_i^*(x_1)$$

2.řád RDM:

$$\gamma_2(x_1' x_2', x_1\, x_2) = \frac{1}{2!} \begin{vmatrix} \gamma_1(x_1' x_1) & \gamma_1(x_2' x_1) \\ \gamma_1(x_1' x_2) & \gamma_1(x_2' x_2) \end{vmatrix} =$$

$$= \frac{1}{2} [\gamma_1(x_1' x_1) \gamma_1(x_2' x_2) - \gamma_1(x_1' x_2) \gamma_1(x_2' x_1)]$$

Lowdin:

$$\gamma_p(x_1^{'}...x_p^{'}, x_1 ... x_p) = \frac{1}{2!} \begin{vmatrix} \gamma_1(x_1^{'}x_1) & ... & \gamma_1(x_p^{'}x_1) \\ ... & ... & ... \\ \gamma_1(x_1^{'}x_p) & ... & \gamma_1(x_p^{'}x_p) \end{vmatrix}$$

p!

$$\hat{\gamma}_1 . \hat{\gamma}_1 = \hat{\gamma}_1 \qquad Tr(\hat{\gamma}_1) = N$$

$$\left[\int \gamma_1[x_1^{'}, x_1^{''}] \gamma_1[x_1^{''}, x_1] dx_1^{''} = \gamma_1(x_1^{'}x_1) \right]$$

$$\int \gamma_1(x_1^{'}x_1) dx_1 = 1$$

N

Hartree-Fock

$$E_{HF}[\gamma_1] = \int [(-\frac{1}{2}\nabla_1^2 + v(x_1))\gamma_1(x_1^{'}, x_1)]_{x_1^{'}=x_1} dx_1 +$$

$$+\frac{1}{2}\iint \frac{1}{r_{12}}[\gamma_1(x_1, x_1)\gamma_1(x_2, x_2) - \gamma_1(x_1, x_2)\gamma_1(x_2, x_1)]dx_1 dx_2$$

$$\delta\{E_{HF}[\gamma_1] - \iint dx_1^{'} dx_1 \alpha(x_1 x_1^{'})\left[\int \gamma_1(x_1^{'}, x_1^{''})\gamma_1(x_1^{''}, x_1)dx_1^{''} - \gamma_1(x_1^{'}, x_1)\right]$$

$$-\beta\left[\int \delta(x_1^{'} - x_1)\gamma_1(x_1^{'}, x_1)dx_1^{'} dx_1 - N\right]\} = 0$$

$$F(x_1, x_1^{'}) - \int dy_1 \alpha(y_1, x_1^{'})\gamma_1(x_1, y_1) - \int dz_1 \alpha(x_1, z_1)\gamma_1(z_1, x_1^{'}) +$$

$$+\alpha(x_1, x_1^{'}) - \beta\delta(x_1^{'} - x_1) = 0$$

kde

$$F(x_1, x_1^{'}) = \frac{\delta E_{HF}[\gamma]}{\delta \gamma(x_1^{'}, x_1)} =$$

$$= \left(-\frac{1}{2}\nabla_1^2 + v(x_1) \right) \delta_1(x_1^{'} - x_1) +$$

$$+\delta_1(x_1^{'} - x_1) \int \frac{1}{r_{12}} \gamma_1(x_2, x_2) dx_2 - \frac{1}{r_{12}} \gamma_1(x_1, x_1^{'})$$

$$\hat{\mathrm{F}} - \hat{\gamma}\hat{\alpha} - \hat{\alpha}\hat{\gamma} + \hat{\alpha} - \beta\hat{1} = 0$$ / $\hat{\gamma}$ zprava; / $\hat{\gamma}$ zleva

a odečtením:

$$\hat{\mathrm{F}}\hat{\gamma} - \hat{\gamma}\hat{\mathrm{F}} = 0$$ $\Leftrightarrow$ $\hat{\gamma}$ a $\hat{\mathrm{F}}$ komutují a spol. vl. fce

Bezspinová hustota ρ <-> γ

$$T[\rho_1] = \int \left[-\frac{1}{2} \nabla^2 \rho_1(r_1^{'}, r_1) \right]_{r_1^{'} = r_1} dr_1$$

$$V_{nl}[\rho] = \int v(r)\rho(r)$$

$$J[\rho_1] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho_1(r_1)\rho_1(r_2) dr_1 dr_2$$

$$K[\rho_1] = \sum_{\sigma}^{2} \frac{1}{2} \iint \frac{1}{r_{12}} \rho_1^{\sigma\sigma}(r_1, r_2)\rho_1^{\sigma\sigma}(r_2, r_1) dr_1 dr_2$$

$\rho_1^{\sigma\sigma}(r_1, r_2) = \frac{1}{2}\rho_1(r_1, r_2)$ [closed shell] → $K[\rho] = \frac{1}{4}\iint \frac{1}{r_{12}} \ldots$

Pak $$\rho_{xc}^{HF}(r_1, r_2) = \rho_x^{HF}(r_1, r_2) = -\frac{1}{2}\frac{\left|\rho(r_1, r_2)\right|^2}{\rho(r_1)}$$ [closed shell]

a $$h^{HF}(r_1, r_2) = -\frac{1}{4}\frac{\left|\rho(r_1, r_2)\right|^2}{\rho(r_1)\rho(r_2)}$$ "exchange hole"

$$\int \rho(r_2) h^{HF}(r_1, r_2) dr_2 = \int \rho_x^{HF}(r_2) dr_2 = -1$$