TRESC数学

$$(\sigma\cdot P)V(\sigma\cdot P)$$
$$= I_2 P_x V P_x + I_2 P_y V P_y + I_2 P_z V P_z$$
$$+ i\sigma_z (P_x V P_y - P_y V P_x)$$
$$+ i\sigma_y (P_x V P_z - P_z V P_x)$$
$$+ i\sigma_x (P_y V P_z - P_z V P_y)$$

$$\sqrt{\frac{\epsilon_i\epsilon_j}{\epsilon_k}}(\sigma\cdot P)V\sqrt{\frac{\epsilon_i\epsilon_j}{\epsilon_k}}(\sigma\cdot P)$$ V的两边对称,算符厄米

$$= I_2\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x V\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x + I_2\sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y V\sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y + I_2\sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z V\sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z$$
$$+ i\sigma_z\left(\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x V\sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y - \sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y V\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x\right)$$
$$+ i\sigma_y\left(\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x V\sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z - \sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z V\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x\right)$$
$$+ i\sigma_x\left(\sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y V\sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z - \sqrt{\frac{\epsilon_x\epsilon_y}{\epsilon_z}}P_z V\sqrt{\frac{\epsilon_x\epsilon_z}{\epsilon_y}}P_y\right)$$

$$\epsilon_x = \frac{1}{\sqrt{1-\frac{c^2}{\epsilon^2}P_x^2}} = 1 + \frac{P_x^2}{2c^2}$$ (到 c^{-2} 阶)

$$\therefore \sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}} = 1 + \frac{P_y^2}{4c^2} + \frac{P_z^2}{4c^2} - \frac{P_x^2}{4c^2} = 1 + \frac{1}{4c^2}(P^2 - 2P_x^2)$$ (到 c^{-2} 阶)

以 $\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x V\sqrt{\frac{\epsilon_y\epsilon_z}{\epsilon_x}}P_x$ 为例,化为:

$$\left[1+\frac{1}{4c^2}(P^2-2P_x^2)\right]P_x V\left[1+\frac{1}{4c^2}(P^2-2P_x^2)\right]P_x$$

$$\left[1+\frac{1}{4c^2}(p^2-2p_x^2)\right]p_x V\left[1+\frac{1}{4c^2}(p^2-2p_x^2)\right]p_x$$

$$=p_xVp_x+\frac{1}{4c^2}(p^2-2p_x^2)p_xVp_x+\frac{1}{4c^2}p_xVp_x(p^2-2p_x^2)$$ (到 c^{-2} 阶)

$$=p_xVp_x+\frac{1}{4c^2}p^2p_xVp_x+\frac{1}{4c^2}p_xVp_x\,p^2$$

$$-\frac{1}{2c^2}p_x^2p_xVp_x-\frac{1}{2c^2}p_xVp_x^2p_x$$

p^2用 $\langle p^2\rangle$本征空间描述.

所以要算的有:

p_xVp_x、p_yVp_y、p_zVp_z、$p_x^3Vp_x$、$p_xVp_x^3$、$p_y^3Vp_y$、$p_yVp_y^3$、$p_z^3Vp_z$、$p_zVp_z^3$

p_xVp_y、p_yVp_x、$p_x^3Vp_y$、$p_xVp_y^3$、$p_y^3Vp_x$、$p_yVp_x^3$

p_xVp_z、p_zVp_x、$p_x^3Vp_z$、$p_xVp_z^3$、$p_z^3Vp_x$、$p_zVp_x^3$

p_zVp_y、p_yVp_z、$p_z^3Vp_y$、$p_zVp_y^3$、$p_y^3Vp_z$、$p_yVp_z^3$

共27个pVp矩阵元! 这些矩阵元之间不可约分.

$$(\langle\chi_i|p_xVp_z|\chi_j\rangle)^\dagger\overset{\text{实}}{=}p_xVp_z|_{ij}$$

$$=\langle\chi_j|p_zVp_x|\chi_i\rangle$$

$$=p_zVp_x|_{ji}$$

$$(\langle\chi_i|p_x^3Vp_z|\chi_j\rangle)^\dagger\overset{\text{实}}{=}p_x^3Vp_z|_{ij}$$

$$=\langle\chi_j|p_zVp_x^3|\chi_i\rangle$$

$$=p_zVp_x^3|_{ji}$$

pVp 和 p^3Vp、pVp^3
都是非对称实矩阵
但都只需算半对角.

$\langle \chi_i | P_x V P_z | \chi_j \rangle$

$= \langle \chi_i | (-i\partial_x)^\dagger V - i\partial_z | \chi_j \rangle$

$= \langle \chi_i | -i\partial_x V - i\partial_z | \chi_j \rangle$

$= -\langle \chi_i | \partial_x V \partial_z | \chi_j \rangle$

P^2、PVP 要取负

$\langle \chi_i | P_x^3 V P_z | \chi_j \rangle$

$= \langle \chi_i | (-i\partial_x)^{3\dagger} V - i\partial_z | \chi_j \rangle$

$= \langle \chi_i | -i \cdot (-\partial_x^3) V - i\partial_z | \chi_j \rangle$

$= \langle \chi_i | \partial_x^3 V \partial_z | \chi_j \rangle$

P^3VP、PVP^3 不取负.

注意: $\langle \chi_i | \partial_x^\dagger \partial_x | \chi_j \rangle = \int dx \langle \chi_i | \partial_x^\dagger | x \rangle \langle x | \partial_x | \chi_j \rangle$

$= \int dx \left(\frac{\partial}{\partial x}\chi_i(x)\right)\left(\frac{\partial}{\partial x}\chi_j(x)\right)$

$\langle \chi_i | \partial_x \partial_x | \chi_j \rangle = \int dx \langle \chi_i | x \rangle \langle x | \frac{\partial^2}{\partial x^2} | \chi_j \rangle$

$= \int dx\, \chi_i(x) \frac{\partial^2}{\partial x^2} \chi_j(x)$

$= \int d\left(\frac{\partial}{\partial x}\chi_j(x)\right) \chi_i(x)$

$= \chi_i(x) \frac{\partial}{\partial x}\chi_j(x) \Big|_{-\infty}^{+\infty} - \int dx \frac{\partial}{\partial x}\chi_j(x) \frac{\partial}{\partial x}\chi_i(x)$

$\overset{\text{边条}}{=} -\int dx \frac{\partial}{\partial x}\chi_j(x) \frac{\partial}{\partial x}\chi_i(x)$

$= -\langle \chi_i | \partial_x^\dagger \partial_x | \chi_j \rangle$

所以用两边作用方式计算的其实正是 $-\nabla^2$ 阵, 不用再取负.

故: $\langle \chi_i | P_x V P_z | \chi_j \rangle = -\langle \chi_i | \partial_x V \partial_z | \chi_j \rangle = \langle \chi_i | \partial_x^\dagger V \partial_z | \chi_j \rangle$ P^2、pVp 不取负

$\langle \chi_i | P_x^3 V P_z | \chi_j \rangle = \langle \chi_i | \partial_x^3 V \partial_z | \chi_j \rangle = -\langle \chi_i | \partial_x^{3\dagger} V \partial_z | \chi_j \rangle$ p^3Vp、pVp^3 要取负

$x_i \to x_j$ transfer formula:

$$I_x(n_i, n_j) = I_x(n_i+1, n_j-1) + (x_i - x_j) I_x(n_i, n_j-1)$$

$$I_x(n_i, n_j-1) = I_x(n_i+1, n_j-2) + (x_i - x_j) I_x(n_i, n_j-2)$$

$$\vdots$$

$$I_x(n_i, 1) = I_x(n_i+1, 0) + (x_i - x_j) I_x(n_i, 0)$$

$$\therefore I_x(n_i, n_j) = I_x(n_i+2, n_j-2) + 2(x_i - x_j) I_x(n_i+1, n_j-2) + (x_i - x_j)^2 I_x(n_i, n_j-2)$$

$$= I_x(n_i+3, n_j-3) + 3(x_i - x_j) I_x(n_i+2, n_j-3) + 3(x_i - x_j)^2 I_x(n_i+1, n_j-3) + (x_i - x_j)^3 I_x(n_i, n_j-3)$$

$$= I_x(n_i+4, n_j-4) + 4(x_i - x_j) I_x(n_i+3, n_i-4) + 6(x_i - x_j)^2 I_x(n_i+2, n_j-4) + 4(x_i - x_j)^3 I_x(n_i+1, n_j-4) + (x_i - x_j)^4 I_x(n_i, n_j-4)$$

binomial coffecient.

$$\vdots$$

j分量
不是k分量

$$I_x(n_i, n_j) = \sum_{k=0}^{n_j} C_{n_j}^{k} (x_i - x_j)^k I_x(n_i + n_j - k, 0)$$

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$$\int_{-\infty}^{+\infty} e^{-b(x-x_0)^2}dx = \sqrt{\frac{\pi}{b}}$$

Gaussian Production Rule.

$$e^{-b_1(x-x_1)^2}e^{-b_2(x-x_2)^2} = e^{-(b_1+b_2)(x-x_p)^2}e^{-\left(\frac{(x_1-x_2)^2}{\frac{1}{b_1}+\frac{1}{b_2}}\right)}$$

$$x_p = \frac{x_2\frac{1}{b_1}+x_1\frac{1}{b_2}}{\frac{1}{b_1}+\frac{1}{b_2}} = \frac{x_2b_2+x_1b_1}{b_1+b_2}$$

s-shell x:

$$\frac{2}{\sqrt{\pi}}\int_0^\infty du\int_{-\infty}^{\infty}dx\ e^{-b_i(x-x_i)^2}e^{-b_j(x-x_j)^2}e^{-b_k(x'-x_k)^2}e^{-b_l(x'-x_l)^2}e^{-u^2(x_1-x_2)^2}$$

$$=\frac{2}{\sqrt{\pi}}e^{-G_x}\int_0^\infty du\int_{-\infty}^{\infty}dx\ e^{-A(x-x_A)^2}e^{-B(x'-x_B)^2}e^{-u^2(x-x')^2}$$

积x:

$$=\frac{2}{\sqrt{\pi}}e^{-G_x}\int_0^\infty du\int_{-\infty}^{\infty}dx'\sqrt{\frac{\pi}{A+u^2}}e^{-\frac{Au^2}{A+u^2}(x'-x_A)^2}e^{-B(x'-x_B)^2}$$

积x':

$$=\frac{2}{\sqrt{\pi}}e^{-G_x}\int_0^\infty du\sqrt{\frac{\pi}{A+u^2}}\sqrt{\frac{\pi}{\frac{Au^2}{A+u^2}+B}}\ e^{-\frac{u^2AB}{AB+u^2A+u^2B}(x_A^2-x_B^2)}$$

$u \to t$ XYZ都有

$$=2e^{-G_x}\sqrt{\frac{\rho}{\pi}}\int_0^1 dt\left(\frac{1}{1-t^2}\right)^{\frac{3}{2}}\frac{\pi}{\sqrt{AB}}\sqrt{1-t^2}\,e^{-D_xt^2}$$

$$=2e^{-G_x}\sqrt{\frac{\rho}{\pi}}\int_0^1 dt\frac{\pi}{\sqrt{AB}}e^{-D_xt^2}$$

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Hess的RI算法是否靠谱?

假设基组$|\chi_i\rangle$完备,经Ω作用得到p^2空间本征态.

$$\Omega|\chi_i\rangle=|p_i\rangle\ ,\ \langle p_i|\hat{p}^2|p_j\rangle=p_i^2 s_i\delta_{ij}$$

考虑到基组$|\chi_i\rangle$不是归一化的,所以我们不能保证$|p_i\rangle$是归一化的(但可以保证正交).故多出重叠积分项$\langle p_i|p_j\rangle=s_i\delta_{ij}$

厄米算符不同本征值的本征态正交.

对于任意算符矩阵$\langle p_i|\hat{A}|p_j\rangle$,有:

$$\langle p_i|\hat{A}|p_j\rangle=\langle\chi_i|\Omega^\dagger\hat{A}\Omega|\chi_j\rangle=\iint dx_1dx_2\langle\chi_i|x_1\rangle\Omega^\dagger\underbrace{\langle x_1|\hat{A}|x_2\rangle}_{=\hat{A}_x\delta_{x_1x_2}}\Omega\langle x_2|\chi_j\rangle=\int dx\langle\chi_i|x\rangle\Omega^\dagger\langle x|\hat{A}|x\rangle\Omega\langle x|\chi_j\rangle$$

并非对$|\chi\rangle$的幺正变换

现在我们希望向复合算符矩阵中插入Identity:

$$\hat{I}|\psi\rangle=\hat{I}\sum_n f_n|p_n\rangle=\sum_{mn}f_n|p_m\rangle\langle p_m|p_n\rangle=\sum_n s_nf_n|p_n\rangle\neq|\psi\rangle$$

所以我们必须将Identity算符修正为:

$$\hat{I}=\sum_m\frac{1}{s_m}|p_m\rangle\langle p_m|\quad\text{------}\ ①$$

故对复合算符矩阵的简单化操作为:

$$\langle p_i|\hat{A}\hat{B}|p_j\rangle=\sum_m\langle p_i|\hat{A}|p_m\rangle\langle p_m|\hat{B}|p_j\rangle/s_m\quad\text{------}\ ②$$

另外一种更常见的场景是,我们首先算算符$\hat{A}$在原基组下矩阵$\langle\chi_i|\hat{A}|\chi_j\rangle$,然后再将之对角化(求本征矢),这样得到的实际上并不是算符$\hat{A}$本征空间表示,很容易证明对于酉变换Ω:

$$\langle\chi_j|\Omega^\dagger\hat{A}\Omega|\chi_i\rangle=\langle\chi_j|\sum_{j=1}^N c_{j\mu}\hat{A}\sum_{i=1}^N c_{\nu i}|\chi_i\rangle\neq\sum_{j=1}^N\sum_{i=1}^N c_{\mu j}\langle\chi_j|\hat{A}|\chi_i\rangle c_{i\nu}=\Omega^\dagger\langle\chi_j|\hat{A}|\chi_i\rangle\Omega$$

而且,对于非正交基$\langle\chi_i|\chi_j\rangle\neq s_i\delta_{ij}$,无法通过酉变换使之成为Hermitain算符本征矢(酉变换是保内积的),这明显与$\Omega^\dagger\langle\chi_i|\hat{A}|\chi_j\rangle\Omega$可以实现对角化相悖。但是,这种"外对角化"的操作也确实可以简化复杂算符矩阵的计算,如DKH Hamiltonian中对p^2矩阵元的外对角化。

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外对角化插入的Identity可以表示为　　$|\chi_m\rangle\Omega \neq \Omega|\chi_m\rangle$，区别于本征矢的Identity.

$$\hat{I}|\psi\rangle=\hat{I}\sum_n f_n|\chi_n\rangle=\sum_{mn}f_n\frac{|\chi_m\rangle\Omega\Omega^{\dagger}\langle\chi_m|}{S_{mm}}\chi_n\rangle=\sum_n f_n\left(\sum_m\frac{S_{mn}|\chi_m\rangle}{S_{mm}}\right)\simeq\sum_n f_n|\chi_n\rangle=|\psi\rangle$$

$$\therefore \hat{I}=\sum_m\frac{1}{S_m}|\chi_m\rangle\langle\chi_m|\ ,\ S_m=\langle\chi_m|\chi_m\rangle\ \cdots\cdots ③$$

所以仍然可以通过②式对复合算符矩阵元简单化，这样操作前提是接受基组不正交引起的误差.

除非我们效仿Hamiltonian的对角化方法，借助Löwdin对称正交化处理 P^2 和其它矩阵，这样就可插入一个真正的Identity:

$$I=\sum_m|\chi_m\rangle S^{-\frac{1}{2}}\Omega\Omega^{\dagger}(S^{-\frac{1}{2}})^{\dagger}\langle\chi_m|$$

注意此处 Ω 变成对 $(S^{-\frac{1}{2}})^{\dagger}\langle P^2\rangle(S^{-\frac{1}{2}})$ 的对角化矩阵，而且这样处理后单电子fock矩阵就不需要再进行Lowdin正交化操作了。$S^{-\frac{1}{2}}$ 求法：设 $U^{\dagger}SU=\Lambda$，$\Lambda=\begin{pmatrix}\lambda_1 & & \\ & \ddots & \\ & & \lambda_n\end{pmatrix}$，则 $\Lambda^{-\frac{1}{2}}=\begin{pmatrix}\lambda_1^{-\frac{1}{2}} & & \\ & \ddots & \\ & & \lambda_n^{-\frac{1}{2}}\end{pmatrix}$，则有:

$$(U\Lambda^{-\frac{1}{2}}U^{\dagger})(U\Lambda^{-\frac{1}{2}}U^{\dagger})=U\Lambda^{-1}U^{\dagger}\overset{U^{\dagger}=U^{-1}}{=\!=\!=}(U\Lambda U^{\dagger})^{-1}=S^{-1}$$

因此 $\underset{\text{Lowdin}^{\dagger}}{U^{\dagger}}\Lambda^{-\frac{1}{2}}\underset{\text{Lowdin}}{U}$ 即所求矩阵.

$S_{0.5}$ 是对称阵.

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复密度矩阵计算

$$
\left.\begin{aligned}
\sum_j^{occ} C_{\sigma j} C^*_{\lambda j} &= \sum_j^{occ} (R_{\sigma j} + i I_{\sigma j})(R_{\lambda j} - i I_{\lambda j}) \\
&= \sum_j^{occ} R_{\sigma j} R_{\lambda j} - i I_{\lambda j} R_{\sigma j} + i I_{\sigma j} R_{\lambda j} + I_{\sigma j} I_{\lambda j} \\
\sum_j^{occ} C_{\lambda j} C^*_{\sigma j} &= \sum_j^{occ} R_{\lambda j} R_{\sigma j} + i I_{\lambda j} R_{\sigma j} - i I_{\sigma j} R_{\lambda j} + I_{\lambda j} I_{\sigma j}
\end{aligned}\right\} \text{厄米} \checkmark
$$

$$
\left.\begin{aligned}
\sum_j^{occ} C_{\sigma j} C^*_{j\lambda} &= \sum_j^{occ} (R_{\sigma j} + i I_{\sigma j})(R_{j\lambda} - i I_{j\lambda}) \\
&= \sum_j^{occ} R_{\sigma j} R_{j\lambda} - i I_{j\lambda} R_{\sigma j} + i I_{\sigma j} R_{j\lambda} + I_{\sigma j} I_{j\lambda} \\
\sum_j^{occ} C_{\lambda j} C^*_{j\sigma} &= \sum_j^{occ} R_{\lambda j} R_{j\sigma} + i I_{\lambda j} R_{j\sigma} - i I_{j\sigma} R_{\lambda j} + I_{\lambda j} I_{j\sigma}
\end{aligned}\right\} \text{不厄米}
$$

复密度矩阵下的PG2计算

$$PG2 = \sum_{\mu\nu} \rho_{\mu\nu} G_{\nu\mu} = \cdots + \rho_{\mu\nu} G_{\nu\mu} + \cdots + \rho_{\nu\mu} G_{\mu\nu} + \cdots$$

其中 $\rho_{\mu\nu} G_{\nu\mu} + \rho_{\nu\mu} G_{\mu\nu} = (\rho^R_{\mu\nu} + i\rho^I_{\mu\nu})(G^R_{\nu\mu} + iG^I_{\nu\mu}) + (\rho^R_{\nu\mu} + i\rho^I_{\nu\mu})(G^R_{\mu\nu} + iG^I_{\mu\nu})$

$$\overset{\rho.G\text{厄米}}{=\!=\!=} (\rho^R_{\mu\nu} + i\rho^I_{\mu\nu})(G^R_{\nu\mu} + iG^I_{\nu\mu}) + (\rho^R_{\mu\nu} - i\rho^I_{\mu\nu})(G^R_{\nu\mu} - iG^I_{\nu\mu})$$

$$= \underbrace{\rho^R_{\mu\nu} G^R_{\nu\mu} - \rho^I_{\mu\nu} G^I_{\nu\mu}} + \underbrace{\rho^R_{\nu\mu} G^R_{\mu\nu} - \rho^I_{\nu\mu} G^I_{\mu\nu}}$$

实部保留,虚部抵消.

开壳层GGA泛函的KS矩阵元计算.

已知: $E^{XC}=\int \varepsilon\left(\rho_\alpha(\vec{r}),\rho_\beta(\vec{r}),\sigma_{\alpha\alpha}(\vec{r}),\sigma_{\alpha\beta}(\vec{r}),\sigma_{\beta\beta}(\vec{r})\right)d\vec{r}$

其中 $\sigma_{\alpha\beta}=\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}\rho_\beta$ ---

且有 $V_\alpha^{XC}=\dfrac{\delta E_{XC}}{\delta\rho_\alpha(\vec{r})}$, $V_\beta^{XC}=\dfrac{\delta E_{XC}}{\delta\rho_\beta(\vec{r})}$

$$F_{\mu\nu}^{XC\alpha}=\int\chi_\mu V_\alpha^{XC}\chi_\nu d\vec{r},\quad F_{\mu\nu}^{XC\beta}=\int\chi_\mu V_\beta^{XC}\chi_\nu d\vec{r}$$

以计算V_α^{XC}为例, 对ρ_α施加微小扰动$\delta\rho_\alpha$, 导致$\sigma_{\alpha\alpha}$, $\sigma_{\alpha\beta}$, $\sigma_{\beta\beta}$变化为:

$$\delta\sigma_{\alpha\alpha}=2\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}(\delta\rho_\alpha)\qquad\delta\sigma_{\alpha\beta}=\vec{\nabla}\rho_\beta\cdot\vec{\nabla}(\delta\rho_\alpha)\qquad\delta\sigma_{\beta\beta}=0$$

则有:

$$\delta E_\alpha^{XC}=\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\rho_\alpha}\delta\rho_\alpha+2\frac{\partial\varepsilon}{\partial\sigma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}(\delta\rho_\alpha)+\frac{\partial\varepsilon}{\partial\sigma_{\alpha\beta}}\vec{\nabla}\rho_\beta\cdot\vec{\nabla}(\delta\rho_\alpha)\right]$$

借助关系 $\vec{\nabla}\cdot(f\vec{A})=f(\vec{\nabla}\cdot\vec{A})+\vec{A}\cdot(\vec{\nabla}f)$, 有:

$$\int d\vec{r}\left[2\frac{\partial\varepsilon}{\partial\sigma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}(\delta\rho_\alpha)\right]$$

$$=\oint d\vec{s}\left[\vec{\nabla}\cdot\left(\delta\rho_\alpha 2\frac{\partial\varepsilon}{\partial\sigma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)\right]-\int d\vec{s}\,\delta\rho_\alpha\vec{\nabla}\cdot\left(2\frac{\partial\varepsilon}{\partial\sigma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)$$

$$=-\int d\vec{r}\,\delta\rho_\alpha\vec{\nabla}\cdot\left(2\frac{\partial\varepsilon}{\partial\sigma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)$$

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另有 $\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\cdot\vec{\nabla}(\delta\rho_\alpha)\right]$

$$=\oint d\vec{s}\left[\vec{\nabla}\cdot\left(\delta\rho_\alpha\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)\right]-\int d\vec{s}\,\delta\rho_\alpha\vec{\nabla}\cdot\left(\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)$$

$$=-\int d\vec{r}\,\delta\rho_\alpha\vec{\nabla}\cdot\left(\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)$$

$$\therefore\ \frac{\delta E_\alpha^{xc}}{\delta\rho_\alpha}=\frac{\partial\varepsilon}{\partial\rho_\alpha}-\vec{\nabla}\cdot\left(2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)-\vec{\nabla}\cdot\left(\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)$$

故:

$$F_{\mu\nu}^{xc\alpha}=\int\chi_\mu V_\alpha^{xc}\chi_\nu d\vec{r}$$

$$=\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\rho_\alpha}-\vec{\nabla}\cdot\left(2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)-\vec{\nabla}\cdot\left(\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)\right]\chi_\mu\chi_\nu$$

再次借助关系 $\vec{\nabla}\cdot(f\vec{A})=f(\vec{\nabla}\cdot\vec{A})+\vec{A}\cdot(\vec{\nabla}f)$，有:

$$\int d\vec{r}\left[-\vec{\nabla}\cdot\left(2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)\chi_\mu\chi_\nu\right]$$

$$=-\oint d\vec{s}\left[\vec{\nabla}\cdot\left(\chi_\mu\chi_\nu 2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\right)\right]+\int d\vec{r}\left[2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

$$=\int d\vec{r}\left[2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

另有 $\int d\vec{r}\left[-\vec{\nabla}\cdot\left(\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)\chi_\mu\chi_\nu\right]$

$$=-\oint d\vec{s}\left[\vec{\nabla}\cdot\left(\chi_\mu\chi_\nu\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)\right]+\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

$$=\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

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综上：

$$F_{\mu\nu}^{xc\alpha}=\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\rho_\alpha}\chi_\mu\chi_\nu+\left(2\frac{\partial\varepsilon}{\partial\gamma_{\alpha\alpha}}\vec{\nabla}\rho_\alpha+\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\beta\right)\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

$$F_{\mu\nu}^{xc\beta}=\int d\vec{r}\left[\frac{\partial\varepsilon}{\partial\rho_\beta}\chi_\mu\chi_\nu+\left(2\frac{\partial\varepsilon}{\partial\gamma_{\beta\beta}}\vec{\nabla}\rho_\beta+\frac{\partial\varepsilon}{\partial\gamma_{\alpha\beta}}\vec{\nabla}\rho_\alpha\right)\cdot\vec{\nabla}(\chi_\mu\chi_\nu)\right]$$

日期：　/

不同基组初猜波函数投影.

$$|\psi_i^B\rangle=\sum_\mu C_{\mu i}^B|\chi_\mu^B\rangle$$

$$|\psi_i^A\rangle=\sum_\nu C_{\nu i}^A|\chi_\nu^A\rangle$$

$$|\psi_i^B\rangle\simeq|\psi_i^A\rangle$$

$$\sum_\mu C_{\mu i}^B|\chi_\mu^B\rangle\simeq\sum_\nu C_{\nu i}^A|\chi_\nu^A\rangle$$

$$\sum_\mu C_{\mu i}^B\langle\chi_\lambda^B|\chi_\mu^B\rangle\simeq\sum_\nu C_{\nu i}^A\langle\chi_\lambda^B|\chi_\nu^A\rangle$$

$$C_B S_{BB}\simeq C_A S_{BA}$$

正交归一性:

$$\begin{aligned}C_B^T S_{BB} C_B &= C_A^T S_{AB} S_{BB}^{-1} S_{BB} S_{BB}^{-1} S_{BA} C_A\\ &= C_A^T S_{AB} S_{BB}^{-1} S_{BA} C_A\\ &\neq I\end{aligned}$$

因此投影后的轨道需要正交化，即对初猜MO做正交化:

$$X^T C_B^T S_{BB} C_B X = I$$

这跟对重叠矩阵(AO)正交化不同，后者是 $X S_{BB} X^T=I$，只有当 $C_B^T C_B=I$ 时二者才等价，如果是SCF时通过Fock对角化得到的MO，满足 $C_B^T C_B=I$，所以只要对S对角化；而上面投影得到的MO并不满足此关系。

这个正交化就用对称正交化(Löwdin方法)，因为我认为已收敛的MO满足Pauli反对称，不太可能出现2条MO几乎相同使X不满秩(即线性相关问题).

日期:　　/

Hartree-Fock与Kohn-Sham的Fock/KS矩阵与电子能

① Hartree-Fock:

$$Fock = h + (J-K)$$

$$E_{ele} = h + \frac{1}{2}\sum^{SO}(J-K) = \sum^{SO}E_{orb} - \frac{1}{2}\sum^{SO}(J-K)$$

② Kohn-Sham

$$Fock = h + J - xK + (1-x)X + C$$

$$E_{ele} = h + \frac{1}{2}\sum^{SO}J - \frac{1}{2}x\sum^{SO}K + (1-x)X + C$$

$$= h + \sum^{SO}J - \frac{1}{2}\sum^{SO}J - x\sum^{SO}K + \frac{1}{2}x\sum^{SO}K + (1-x)X + C$$

$$= \sum^{SO}E_{orb} - \frac{1}{2}\sum^{SO}(J-xK)$$

经验证，上式计算得到的Eele与实际电子能不符；就是说实际上，XC能量不具备轨道的加和性质，它不与轨道直接关联而是与整体波函数(密度)关联。KS电子能唯一算法是 $E_{ele} = h + \frac{1}{2}\sum^{SO}J - \frac{1}{2}x\sum^{SO}K + (1-x)X + C$

DFT计算不能仅靠分析轨道得到结论，分子的性质不是仅由轨道决定。

日期:　　/

高速运动系下二分量MO坐标与自旋的观测值.

已知静止系的可观测量,求运动系的可观测量,必须经历Lorentz变换;其中的关键是,必须以运动系的"同时"($\Delta t=0$)为前提,即:

$$X_{rest} = \Lambda(X_{motion})|_{\Delta t=0}$$

这必须对Lorentz矩阵的空间部分(3×3)求逆,先列出正向变换的空间部分可写作:

$$\begin{aligned} L &= I + \frac{\gamma-1}{\beta^2}(\vec{\beta}\vec{\beta}^T) \\ &= I + kM \end{aligned}$$

根据Sherman公式:

$$\begin{aligned} (I+kM)^{-1} &= I - \frac{kM}{1+k\,tr(M)} \\ &= I - \frac{\frac{\gamma-1}{\beta^2}\beta\beta^T}{1+\frac{\gamma-1}{\beta^2}\beta^2} \\ &= I - \frac{\gamma}{\gamma+1}\beta\beta^T = L^{-1} \end{aligned}$$

此式可方便地求出运动系的波函数空间部分,但自旋部分更复杂,涉及非线性的Imitative变换,直接求逆不容易;反之,可利用其拟向性质,对于静止系中只有z方向不为0的$\vec{s_z}$(0, 0, s),变换后方向必然相等子:

$$\vec{S_z}' = \vec{S_z} - \frac{\gamma}{\gamma+1}\beta_3 s\vec{\beta}$$

其模方为：

$$\vec{S_z}'^2 = \frac{\gamma^2}{(\gamma+1)^2}\beta_3^2 s^2\beta_1^2 + \frac{\gamma^2}{(\gamma+1)^2}\beta_3^2 s^2\beta_2^2 + \left(s - \frac{\gamma}{\gamma+1}\beta_3^2 s\right)^2$$

$$= s^2\left[\frac{\gamma^2}{(\gamma+1)^2}\beta_3^2\beta_1^2 + \frac{\gamma^2}{(\gamma+1)^2}\beta_3^2\beta_2^2 + \left(1 - 2\frac{\gamma}{\gamma+1}\beta_3^2 + \frac{\gamma^2}{(\gamma+1)^2}\beta_3^4\right)\right]$$

$$= s^2\left[\frac{\gamma^2}{(\gamma+1)^2}\beta_3^2\beta^2 + 1 - \frac{2\gamma}{\gamma+1}\beta_3^2\right]$$

考虑到 $\frac{\gamma^2}{\gamma+1} = \frac{\gamma-1}{\beta^2}$

$$\therefore \vec{S_z}^2 = s^2\left[\frac{\gamma-1}{\gamma+1}\beta_3^2 + 1 - \frac{2\gamma}{\gamma+1}\beta_3^2\right]$$

$$= s^2\left[1-\beta_3^2\right]$$

故考虑Imitative变换后的$\vec{S_z}$为：

$$S_z' = \frac{1-\frac{\gamma}{\gamma+1}\beta_3^2}{\sqrt{1-\beta_3^2}}\, s$$

考虑系数的取值：

$$\left(1-\frac{\gamma}{\gamma+1}\beta_3^2\right)^2 \le 1-\beta_3^2$$

$$1-\frac{2\gamma}{\gamma+1}\beta_3^2 + \frac{\gamma^2}{(\gamma+1)^2}\beta_3^4 \le 1-\beta_3^2$$

$$-\frac{2\gamma}{\gamma+1}+\frac{\gamma^2}{(\gamma+1)^2}\beta_3^2\leq -1$$

$$-2\gamma^2-2\gamma+\gamma^2\beta_3^2\leq -\gamma^2-2\gamma-1$$

$$1-\gamma^2+\gamma^2\beta_3^2\leq 0$$

$$1-\beta^2\leq 1-\beta_3^2$$

此式恒成立，当且仅当$\beta^2=\beta_3^2$时取等，这与Imitative变换定义相符。这一不等式关系表明运动系下自旋态趋于平均化，偏离$\pm\frac{1}{2}$，当运动系趋近光速时，即$\lim_{\beta\to 0} s_z' = \lim_{\beta\to 0}\sqrt{1-\beta_3^2}\, s = 0$，此时电子自旋行为趋近玻色子。

用于反映TRS破缺程度的kappa参数计算.

$\kappa = \| MM^* + I \| = \left[\sum_{ij}(M_{ij}M_{ij}^* + \delta_{ij})^2\right]^{\frac{1}{2}}$ 其中 $M_{ij} = \langle \psi_i | -i\sigma_y | \psi_j \rangle$

标量计算中$\kappa = \sqrt{N_\alpha - N_\beta}$，二分量时对该值的偏差可视为SOC导致的对TRS的偏离.

日期：　/

二分量波函数的旋转群积分（Rotation Group Integration, RGI）

把 $S_{\alpha\beta\gamma}$ 作用到任一旋量轨道 $\begin{pmatrix} S_a \\ S_b \end{pmatrix}$

$$P_{MK}^{S} = \frac{2S+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, D_{MK}^{S*} \cdot e^{-\frac{i}{2}\alpha\sigma_z} e^{-\frac{i}{2}\beta\sigma_y} e^{-\frac{i}{2}\gamma\sigma_z} \begin{pmatrix} S_a \\ S_b \end{pmatrix}$$

$$= \frac{2S+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} e^{im\alpha} d_{mk}^{s} e^{ik\gamma} \begin{pmatrix} e^{-\frac{i}{2}(\alpha+\gamma)}\cos\frac{\beta}{2} S_a - e^{-\frac{i}{2}(\alpha-\gamma)}\sin\frac{\beta}{2} S_b \\ e^{\frac{i}{2}(\alpha-\gamma)}\sin\frac{\beta}{2} S_a + e^{\frac{i}{2}(\alpha+\gamma)}\cos\frac{\beta}{2} S_b \end{pmatrix}$$

上旋量 =

$$\frac{2S+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, e^{im\alpha} d_{mk}^{s} e^{ik\gamma} \left[e^{-\frac{i}{2}(\alpha+\gamma)}\cos\frac{\beta}{2} S_a - e^{-\frac{i}{2}(\alpha-\gamma)}\sin\frac{\beta}{2} S_b \right]$$

$$= \frac{(2S+1)S_a}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, e^{i(m-\frac{1}{2})\alpha} d_{mk}^{s} e^{i(k-\frac{1}{2})\gamma} \cos\frac{\beta}{2}$$

$$- \frac{(2S+1)S_b}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, e^{i(m-\frac{1}{2})\alpha} d_{mk}^{s} e^{i(k+\frac{1}{2})\gamma} \sin\frac{\beta}{2}$$

$$= \frac{(2S+1)S_a}{8\pi^2}\int_0^{2\pi} d\alpha\, e^{i(m-\frac{1}{2})\alpha} \int_0^{\pi} d\beta\, d_{mk}^{s} \sin\beta \cos\frac{\beta}{2} \int_0^{2\pi} d\gamma\, e^{i(k-\frac{1}{2})\gamma}$$

$$- \frac{(2S+1)S_b}{8\pi^2}\int_0^{2\pi} d\alpha\, e^{i(m-\frac{1}{2})\alpha} \int_0^{\pi} d\beta\, d_{mk}^{s} \sin\beta \sin\frac{\beta}{2} \int_0^{2\pi} d\gamma\, e^{i(k+\frac{1}{2})\gamma}$$

明显这种情况在 $M=\frac{3}{2}, \frac{5}{2} \dots$ 时积分值为0，意味着永远不可能投影出 $M=\frac{3}{2}, \frac{5}{2} \dots$ 的态，这不合理。原因在于 P_{MK}^{S} 应作用于整体的多电子态 $|\Phi\rangle$，而非依次作用到轨道上。

把$S_{\alpha\beta\gamma}$作用到旋量态$|\Psi\rangle$上并将投影态与Ψ内积:

$$\langle\Psi|P^S_{MK}|\Psi\rangle=\frac{2S+1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\int_0^{2\pi}d\gamma\,\sin\beta\,D^{S*}_{MK}\cdot\langle\Psi|\hat{U}_{SU2}|\Psi\rangle$$

令旋转后$\hat{U}_{SU2}|\Psi\rangle(\alpha,\beta,\gamma)=|\Phi\rangle(\alpha,\beta,\gamma)$

且 $|\Psi\rangle=\frac{1}{\sqrt{N!}}\det\begin{pmatrix}\psi_1(x_1) & \cdots & \psi_1(x_N)\\ \vdots & \ddots & \vdots\\ \psi_N(x_1) & \cdots & \psi_N(x_N)\end{pmatrix}$ $|\Phi\rangle=\frac{1}{\sqrt{N!}}\det\begin{pmatrix}\phi_1(x_1) & \cdots & \phi_1(x_N)\\ \vdots & \ddots & \vdots\\ \phi_N(x_1) & \cdots & \phi_N(x_N)\end{pmatrix}$

则
$$\begin{aligned}\langle\Psi|P^S_{MK}|\Psi\rangle&=\frac{2S+1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\int_0^{2\pi}d\gamma\,\sin\beta\,D^{S*}_{MK}(\alpha,\beta,\gamma)\cdot\langle\Psi|\Phi\rangle(\alpha,\beta,\gamma)\\&=\frac{2S+1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\int_0^{2\pi}d\gamma\,\sin\beta\,D^{S*}_{MK}(\alpha,\beta,\gamma)\cdot\det(\langle\phi|\psi\rangle)\\&=\frac{2S+1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\int_0^{2\pi}d\gamma\,\sin\beta\,D^{S*}_{MK}(\alpha,\beta,\gamma)\det(\mathrm{oper3}^\dagger_\phi\,\mathrm{oper3}_\psi)\end{aligned}$$

(oper3是正交归一基上的正交归一轨道)

对于二分量单行列式态，要构造S^2和S_z的纯态，首先要从被投影态$|\Psi\rangle$中提取相同S_z的成分，然后旋转投影：对于具有相同S^2但不同S_z的分量，使用Wigner D矩阵D^S_{MK}将其转换为相同S_z会导致态间相互污染。因此，需要对所有可能的M令K=M。

$$\langle\Psi|P^S_{MK}|\Psi\rangle=\frac{2S+1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}d\beta\int_0^{2\pi}d\gamma\,\sin\beta\,e^{iM\alpha}e^{iM\gamma}d^S_{MM}(\beta)\cdot\det(\mathrm{oper3}^\dagger_\phi\,\mathrm{oper3}_\psi)$$

由于Wigner-Eckart定理，只有$|\Delta S|\le 1$且$|\Delta S_z|\le 1$的态之间会发生耦合(只有SOC的情形)，因此在确定了basical configuration后，需要考虑的自旋组态是有限的: