Correlated N-Particle States Totally Determined by One Particle Generalized Spin Orbitals

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Why is the

Independent Particle Model

So useful?

Orbitals $\Leftrightarrow$ Electrons

Pictures of Molecules

⇓

- Understand properties
- Predict and design reactions
- Design materials and drugs

However

The Independent Particle Model can often predict incorrect

- Properties
- Reactions
- Structures

Due to the absence of electron-electron correlation effects

Thus we want a one

electron $\leftrightarrow$ orbital model

that describes correlation effects

Definition of a One Particle Theory

N-particle State **totally determined** by

- A set of orthonormal Generalized Spin Orbitals (GSO's) spanning one particle space

$$\left\{\psi_j(\mathbf{r},\xi);1 \le j \le r\right\}$$

- A set of occupation numbers of these GSO's

$$\left\{N_j;1 \le j \le r\right\}$$

Expectation values are expressed in terms of one particle quantities

Generalized Spin Orbitals

$$\psi_j(\mathbf{r},\xi) = \sum_k \left\{ c_{jk\alpha}\varphi_k(\mathbf{r})\alpha(\xi) + c_{jk\beta}\varphi_k(\mathbf{r})\beta(\xi) \right\}$$

$$\psi_j(\mathbf{r},\xi) = \langle \mathbf{r},\xi | \psi_j \rangle$$

$$\varphi_k(\mathbf{r}) = \langle \mathbf{r} | \varphi_k \rangle$$

$$\alpha(\xi) = \langle \xi | \alpha \rangle$$

$$\beta(\xi) = \langle \xi | \beta \rangle$$

Occupation Number

N_j

is the probability that an electron belonging to a group of N-electrons in a specific N-electron state is somewhere in the region of space/spin associated with the probability distribution

$$\left|\psi_j\left(\mathbf{r},\xi\right)\right|^2$$

GSO's and occupation numbers define a First Order Reduced Density Operator (FORDO)

$$D^1 = \sum_{1 \le j \le r} N_j \left| \psi_j \right\rangle \left\langle \psi_j \right|$$

So is a one particle theory a FORDO theory?

No, as

$$\{\psi_j(\mathbf{r},\xi);1\le j\le r\}\ \&\ \{N_j;1\le j\le r\}$$

is many to one

$$D^1=\sum_{1\le j\le r}N_j\left|\psi_j\right\rangle\left\langle\psi_j\right|$$

Even when $\{N_j;1\le j\le r\}$ are non degenerate

As

$$\left\{ \left| e^{i\theta_j} \psi_j \right\rangle ; 1 \le j \le r \right\}$$

Produce the same FORDO.

Do these GSO's and occupation numbers produce different N electron states?

Yes !

FORDO's

are invariant to U(1)

but N-electron states

are not in general

invariant to U(1)

The reducible representation

$$u\,|\psi\rangle = |\psi\rangle\,\mathbf{u}_\psi$$

$$\mathbf{u}_\psi = \begin{pmatrix} e^{i\alpha_1} & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & e^{i\alpha_r} \end{pmatrix}$$

leaves the FORDO invariant, while the induced representation

$$\bigwedge^{N} \mathbf{u}_\psi$$

does not leave N-particle states invariant

Example of Correlated N Particle States Determined by different sets of GSO's and Occupation Numbers

Antisymmetrized Geminal Power States (AGPs)

$$\left| g^{\frac{N}{2}} \right\rangle$$

$$\Vert$$

$$\sum_{1 \le j_1 < \cdots < j_{\frac{N}{2}} \le s} c_{j_1} \cdots c_{j_{\frac{N}{2}}} \left| \psi_{j_1} \psi_{j_1+s} \cdots \psi_{j_{\frac{N}{2}}} \psi_{j_{\frac{N}{2}}+s} \right\rangle$$

Review of their Properties

Geminal

$$|g\rangle = \sum_{1 \le j \le s} c_j |\psi_j \psi_{j+s}\rangle$$

$c_j \geq 0 =$ Real Canonical Coefficients

$\{|\psi_j\rangle; 1 \le j \le r = 2s\}$ are

Canonical General Spin Orbitals (CGSO's)

that form an orthonormal basis of one electron space

FORDO of $|g\rangle$

$$D^1\left(|g\rangle\langle g|\right)=\sum_{1\le j\le s} n_j\left\{|\psi_j\rangle\langle\psi_j|+|\psi_{j+s}\rangle\langle\psi_{j+s}|\right\}$$

$$n_j=c_j^2$$

Eigenvalues of $|g\rangle\langle g|$ at least doubly degenerate

degeneracy can be greater i.e.

some of the $\{n_j;1\le j\le s\}$ can be equal

FORDO of AGP

$$D^1\left(\left|g^{\frac{N}{2}}\right\rangle\left\langle g^{\frac{N}{2}}\right|\right)=\sum_{1\le j\le s} N_j\left\{\left|\psi_j\right\rangle\left\langle\psi_j\right|+\left|\psi_{j+s}\right\rangle\left\langle\psi_{j+s}\right|\right\}$$

Eigenvalues of $D^1\left(\left|g^{\frac{N}{2}}\right\rangle\left\langle g^{\frac{N}{2}}\right|\right)$ at least doubly degenerate

degeneracy can be greater i.e.

some of the $\left\{N_j;1\le j\le s\right\}$ can be equal.

This leads to interesting physical properties

even superconductivity

CSO's **are** NGSO's

but

NGSO's are

not

necessarily CSO's

A. J. Coleman has proved (Reduced Density Matrices pp 142-144), that

$$\{N_j; 1 \le j \le s\} \leftrightarrow \{n_j; 1 \le j \le s\}$$

in a 1-1 fashion

$$N_j = \frac{n_j S_{\frac{N}{2}-1}\left(\hat{j}\right)}{S_{\frac{N}{2}}}$$

$$S_{\frac{N}{2}} = \sum_{1 \le j_1 < \cdots < j_{\frac{N}{2}} \le s} n_{j_1} \cdots n_{j_{\frac{N}{2}}}$$

$$S_{\frac{N}{2}-1}\left(\hat{j}\right) = \sum_{\substack{1 \le j_1 < \cdots < j_{\frac{N}{2}-1} \le s \\ j \notin \left\{ j_1, \cdots, j_{\frac{N}{2}-1} \right\}}} n_{j_1} \cdots n_{j_{\frac{N}{2}-1}}$$

Thus

$$\{N_j;1\le j\le s\}\text{and}\{\psi_j;1\le j\le r\}$$

$$\Updownarrow$$

$$\{n_j;1\le j\le s\}\text{and}\{\psi_j;1\le j\le r\}$$

$$\Updownarrow$$

$$\{c_j;1\le j\le s\}\text{and}\{\psi_j;1\le j\le r\}$$

$$\Downarrow$$

$$|g\rangle$$

$$\Updownarrow$$

$$\left|g^{\frac{N}{2}}\right\rangle$$

Why the red line?

Geminal and thus the AGP has a non trivial invariance group and many sets of CGSO's correspond to the same geminal and AGP.

The manifold of geminals (thus AGP's) can be parameterized by

$$|g(\mathbf{c},\theta,\psi)\rangle = \sum_{1\leq j\leq s} c_j e^{i\theta_j} |\psi_j \psi_{j+s}\rangle$$

where

$$\{\,|\psi_j\rangle \,|\, 1 \leq j \leq r\}$$

is a complete orthonormal basis

the pairs of CGSO's are representatives of the equivalence classes formed by

$$\{|\psi_a\rangle, |\psi_b\rangle\} \sim \{|\psi_c\rangle, |\psi_d\rangle\}$$
$$|\psi_a\psi_b\rangle\langle\psi_a\psi_b| = |\psi_c\psi_d\rangle\langle\psi_c\psi_d|$$

$$\sum_{1\leq j\leq s} c_j^2 = 1; c_j \geq 0; 1 \leq j \leq s$$

and

$$0 \leq \theta_2, \cdots, \theta_s < 2\pi; \theta_1 = 0$$

hence

$$\left| g^{\frac{N}{2}} \right\rangle$$

is always invariant to

transformations

belonging to the group

$$SU(2)$$

that act on the subspaces

$$V_j = \text{Linear Span} \left\{ \left| \psi_j \right\rangle, \left| \psi_{j+s} \right\rangle \right\}$$

$$1 \leq j \leq s$$

If the occupation numbers of the geminal are more than two fold degenerate then the invariance group of the geminal is bigger than

$$SU(2)$$

Which can describe various physical phenomena e.g. superconductivity

This parameterization shows that geminals are **not** invariant to

$$U(2)$$

But these transformations do leave invariant the

- ❖ canonical coefficients
- ❖ geminal occupation numbers
- ❖ occupation numbers of the FORDO

The manifold of geminals that have the same canonical coefficients has the invariance group

$$U(1) = U(2)/SU(2)$$

leading to the set of AGP's based on

$$\{g(\mathbf{c}, \theta, \psi)\}; 0 \leq \theta_2, \cdots, \theta_s < 2\pi; \theta_1 = 0$$

all having the same FORDO for a fixed (c,ψ).

These however in general produce different N-particle states

$$\left| g\left(\mathbf{c},\theta,\psi\right)^{\frac{N}{2}} \right\rangle$$

$$\|$$

$$\sum_{1\leq j_1<\cdots<j_{\frac{N}{2}}\leq s} c_{j_1}\cdots c_{j_{\frac{N}{2}}} \exp\left\{ i \sum_{1\leq\kappa\leq\frac{N}{2}} \theta_{j_\kappa} \right\} \left| \psi_{j_1}\psi_{j_1+s}\cdots\psi_{j_{\frac{N}{2}}}\psi_{j_{\frac{N}{2}}+s} \right\rangle$$

This can be seen by noting the form of the AGP-Second Order Reduced Density Operator

Second Order Reduced Density Operators (SORDO's)

$$D^2\left(\left|g^{\frac{N}{2}}\right\rangle\left\langle g^{\frac{N}{2}}\right|\right)=\frac{1}{S_{\frac{N}{2}}}\left\{\sum_{1\le j\le s} n_j S_{\frac{N}{2}-1}\left(\hat{j}\right)\left|\psi_j\psi_{j+s}\right\rangle\left\langle\psi_j\psi_{j+s}\right|\right.$$

$$+\sum_{1\le j\ne k\le s} c_j c_k e^{i\left(\theta_j-\theta_k\right)} S_{\frac{N}{2}-1}\left(\hat{j}\hat{k}\right)\left|\psi_j\psi_{j+s}\right\rangle\left\langle\psi_k\psi_{k+s}\right|$$

$$\left.+\sum_{\substack{1\le j<k\le r\\ k\ne j+s}} n_j n_k S_{\frac{N}{2}-2}\left(\hat{j}\hat{k}\right)\left|\psi_j\psi_k\right\rangle\left\langle\psi_j\psi_k\right|\right\}$$

which shows that for fixed (c,ψ) the SORDO's are different unless

$$\theta \sim \theta'$$

where

$$\{\theta_1, \cdots, \theta_s\} \sim \{\theta'_1, \cdots, \theta'_s\}$$

$$0 \leq \theta_j, \theta'_j < 2\pi; 1 \leq j \leq s$$

$$\theta_j - \theta_k = \theta'_j - \theta'_k; 1 \leq j < k \leq s$$

and thus correspond to different N-particle states, that have energies given by

$$\mathcal{E}(\mathbf{n},\psi,\theta)=\frac{\mathcal{H}(\mathbf{n},\psi,\theta)}{S_N(\mathbf{n})}=$$

$$\left\{\sum_{1\le j\le s} n_j S_{N-1}(j)\left\{\langle\psi_j|h_1\psi_j\rangle+\langle\psi_{j+s}|h_1\psi_{j+s}\rangle+\langle\psi_j\psi_{j+s}||\psi_j\psi_{j+s}\rangle\right\}\right.$$

$$+\sum_{1\le j,k\le s}\left\{n_j^{\frac{1}{2}}n_k^{\frac{1}{2}}e^{i(\theta_j-\theta_k)}S_{N-1}(jk)\langle\psi_j\psi_{j+s}||\psi_k\psi_{k+s}\rangle\right.$$

$$\left.\left.+n_in_jS_{N-2}(jk)\langle\psi_j\psi_k|||\psi_j\psi_k\rangle\right\}\right\}\Big/S_N(\mathbf{n})$$

where

$$\langle \psi_j \psi_k | | \psi_j \psi_k \rangle = \langle jk || jk \rangle + \langle j\, k+s || j\, k+s \rangle + \langle j+s\, k || j+s\, k \rangle + \langle j+s\, k+s || j+s\, k+s \rangle ; 1 \leq j,k \leq s.$$

and

$$\langle jk || lm \rangle = \int \left\{ \psi_j^* (\mathbf{r}_1, \xi_1) \psi_k^* (\mathbf{r}_2, \xi_2) \frac{1}{\| \mathbf{r}_1 - \mathbf{r}_2 \|} \psi_l (\mathbf{r}_1, \xi_1) \psi_m (\mathbf{r}_2, \xi_2) - \psi_j^* (\mathbf{r}_1, \xi_1) \psi_k^* (\mathbf{r}_2, \xi_2) \frac{1}{\| \mathbf{r}_1 - \mathbf{r}_2 \|} \psi_l (\mathbf{r}_2, \xi_2) \psi_m (\mathbf{r}_1, \xi_1) \right\} d\mathbf{r}_1 d\mathbf{r}_2 d\xi_1 d\xi_2$$

$$1 \leq j,k \leq 2s; 1 \leq l,m \leq 2s$$

The set of N-particle AGP states can thus be classified into the equivalence classes:

- **Same FORDO**
- **Same SORDO same FORDO**

Correlated N-electron state described by orthogonal but unnormalized GSO’s

We can fold the geminal occupation numbers and phase factors into the normalized CSO's to produce a SORDO and energy expression that just depends on an orthogonal but unnormalized set of CSO's

$$|\eta_j\rangle = n_j^{\frac{1}{2}} e^{i\frac{\theta_j}{2}} |\psi_j\rangle$$

$$\mathcal{E}(\eta) = \frac{\mathcal{H}(\eta)}{S_N(\mathbf{n})} =$$

$$\left\{ \sum_{1\le j\le s} S_{N-1}(j) \left\{ \langle \eta_j | h_1 \eta_j \rangle + \langle \eta_{j+s} | h_1 \eta_{j+s} \rangle + n_j^{-1} \langle \eta_j \eta_{j+s} | | \eta_j \eta_{j+s} \rangle \right\} \right.$$

$$+ \sum_{1\le j,k\le s} \left\{ S_{N-1}(jk) \langle \eta_j \eta_{j+s} | | \eta_k \eta_{k+s} \rangle \right.$$

$$\left. \left. + S_{N-2}(jk) \langle \eta_j \eta_k | | | \eta_j \eta_k \rangle \right\} \right\} \Big/ S_N(\mathbf{n})$$

N-electron energy in terms of one electron quantities

Energy Optimized AGP's

Contains Independent Particle model as a special case

The optimization problem can be expressed in terms of many different sets of parameters, one form is

$$\min_{(\mathbf{n},\varphi)} \mathcal{E}\left(\mathbf{n},\varphi\right)$$

subject to the orthonormality constraints

$$\langle \varphi_j | \varphi_k \rangle = \delta_{jk}; \quad 1 \leq j, k \leq 2s$$

and the constraints of positivity on the geminal occupation numbers

$$n_j \geq 0; \quad 1 \leq j \leq s,$$

where

$$\mathcal{E}(\mathbf{n},\varphi)=\frac{\mathcal{H}(\mathbf{n},\varphi)}{S_N(\mathbf{n})}=$$

$$\left\{\sum_{1\le j\le s} n_j S_{N-1}(j)\left\{\langle\varphi_j|h_1\varphi_j\rangle+\langle\varphi_{j+s}|h_1\varphi_{j+s}\rangle+\langle\varphi_j\varphi_{j+s}||\varphi_j\varphi_{j+s}\rangle\right\}\right.$$

$$+\sum_{1\le j,k\le s}\left\{n_j^{\frac{1}{2}}n_k^{\frac{1}{2}}S_{N-1}(jk)\langle\varphi_j\varphi_{j+s}||\varphi_k\varphi_{k+s}\rangle\right.$$

$$\left.\left.+n_in_jS_{N-2}(jk)\langle\varphi_j\varphi_k|||\varphi_j\varphi_k\rangle\right\}\right\}\Big/S_N(\mathbf{n})$$

The positivity constraint can be removed by

$$\mathcal{E}\left(\alpha,\varphi\right)=\mathcal{E}\left(\mathbf{n}\left(\alpha\right),\varphi\right)$$

where

$$n_j\left(\alpha\right)=e^{\alpha_j}n_{0j}$$

and the constrained optimization over the GSO's can be transformed to an unconstrained optimization using a Lagrangian defined as

$$\mathcal{L}(\alpha,\varphi)=\mathcal{E}(\alpha,\varphi)-\sum_{1\le j,k\le 2s}\varepsilon_{kj}\left(\langle\varphi_j|\varphi_k\rangle-\delta_{jk}\right)$$

$$\text{where }\langle\varphi_k|\varphi_j\rangle=\langle\varphi_j|\varphi_k\rangle^*\Rightarrow\varepsilon_{jk}=\varepsilon_{kj}^*$$

Leading to the unconstrained optimization

$$\mathcal{L}\left(\alpha_\#,\varphi_\#\right)=\min_{(\alpha,\varphi)}\mathcal{L}(\alpha,\varphi)$$

Generalized Fock Operator

The first order stationarity conditions

$$\frac{\partial \mathcal{L}\left(\alpha_{\#}, \varphi_{\#}\right)}{\partial \varphi_j^*} = \frac{\partial \mathcal{L}\left(\alpha_{\#}, \varphi_{\#}\right)}{\partial \varphi_j} = 0$$

$$\frac{\partial \mathcal{L}\left(\alpha_{\#}, \varphi_{\#}\right)}{\partial \alpha_j} = 0; \quad 1 \leq j \leq s$$

and the observation that the GSO derivatives can be expressed using generalized Fock operators as

$$\frac{\partial \mathcal{E}(\alpha,\varphi)}{\partial \varphi_j^*} = F(\mathbf{n},\varphi)\,|\varphi_j\rangle \quad \text{and} \quad \frac{\partial \mathcal{E}(\alpha,\varphi)}{\partial \varphi_j} = \langle\varphi_j|\,F(\mathbf{n},\varphi)^\dagger$$

leads to

$$\frac{\partial \mathcal{E}\left(\mathbf{n}_\#,\varphi_\#\right)}{\partial \varphi_j^*} = F\left(\mathbf{n}_\#,\varphi_\#\right)|\varphi_{\#j}\rangle = \sum_{1\le k\le 2s} |\varphi_{\#k}\rangle\,\varepsilon_{\#kj}$$

and **hence**

$$F\left(\mathbf{n}_\#,\varphi_\#\right) = F\left(\mathbf{n}_\#,\varphi_\#\right)^\dagger$$

The generalized Fock operator for **any** Multi Configurational State (MCS) is given by

$$F\left(\mathbf{C},\varphi\right)=\sum_{1\leq m,n\leq 2s}\left\{\left(\mathbb{H}_1\left(\varphi\right)\mathbb{D}^1\left(\mathbf{C}\right)\right)_{mn}+\frac{1}{2}\left(L_2^1\left(\mathbb{V}_2\left(\varphi\right)\mathbb{D}^2\left(\mathbf{C}\right)\right)\right)_{mn}\right\}\left|\varphi_m\right\rangle\left\langle\varphi_n\right|$$

where **C** are the CI coefficients. As the SORDO for the AGP state **only** depends on the CSO's and the occupation numbers the generalized Fock operator for the AGP state is

$$F\left(\mathbf{n},\varphi\right)=\sum_{1\leq m,n\leq 2s}\left\{\left(\mathbb{H}_1\left(\varphi\right)\mathbb{D}^1\left(\mathbf{n}\right)\right)_{mn}+\frac{1}{2}\left(L_2^1\left(\mathbb{V}_2\left(\varphi\right)\mathbb{D}^2\left(\mathbf{n}\right)\right)\right)_{mn}\right\}\left|\varphi_m\right\rangle\left\langle\varphi_n\right|$$

Where the contraction operator is defined by

$$L_2^1\left(\mathbb{A}\right)_{jk}=\sum_{1\leq l\leq 2s}A_{jlkl}$$

A crucial property in Hartree-Fock theory for IPS's is the invariance of such states to transformations that map occupied GSO's to occupied GSO's i.e.

$$|\Psi_{IPS}\rangle = U_N\,|\Psi_{IPS}\rangle = |U_{orb}\psi_1 \cdots U_{orb}\psi_N\rangle$$

where

$$U_{orb} : \mathcal{H}^1_{occ} \rightarrow \mathcal{H}^1_{occ}$$

$$\mathcal{H}^1_{occ} = \text{linear span}\,\{\,|\psi_j\rangle|\; N_j \neq 0; 1 \leq j \leq 2s\}$$

This allows one to give special significance to the GSO's that diagonalize the IPS Fock operator and their eigenvalues

This invariance can be generalized to MCS's

$$U\left|\Psi\right\rangle = \left|\Psi\left(\mathbb{U}_{CI}\mathbf{C}\left(\psi\right), U_{orb}\psi\right)\right\rangle = \left|\Psi\right\rangle$$

where $\mathbf{C}\left(\psi\right)$ are the C.I. coefficients wrt the basis

$$\left\{\left|\psi_j\right\rangle \middle| \, 1 \leq j \leq 2s\right\}$$

and

$$U_{orb} : \mathcal{H}^1_{occ} \rightarrow \mathcal{H}^1_{occ}$$

$$\mathbb{U}_{CI} : \mathbb{C}^{\binom{2s}{N}} \rightarrow \mathbb{C}^{\binom{2s}{N}}$$

In the special case of an AGP state based on the geminal

$$|g(\mathbf{n},\varphi)\rangle = \sum_{1\leq k,l\leq 2s} g_{kl}(\mathbf{n},\psi)\,|\psi_k\psi_l\rangle = \sum_{1\leq j\leq 2s} n_j^{\frac{1}{2}}\,|\varphi_j\varphi_{j+s}\rangle$$

the invariance transformations are generated by

$$\sum_{1\leq j\leq 2s} n_j^{\frac{1}{2}}\,|\varphi_j\varphi_{j+s}\rangle = \sum_{1\leq k,l\leq 2s} \left(\mathbb{U}\mathbf{n}_2^{\frac{1}{2}}\mathbb{U}^t\right)_{kl}|\psi_k\psi_l\rangle$$

where $\mathbf{n}_2^{\frac{1}{2}} = \begin{pmatrix} \mathbf{n}^{\frac{1}{2}} & \mathbb{0} \\ \mathbb{0} & \mathbf{n}^{\frac{1}{2}} \end{pmatrix}$ and $\varphi_j = U\psi_j$

One can show that for a fully optimized MCSCF state that the diagonal elements of the generalized Fock operator in **any** basis

$$\{\,|\psi_j\rangle|\,1 \leq j \leq 2s\}$$

are

$$F\left(\mathbf{C}\left(\psi\right),\psi\right)_{jj} = \Xi_j\left(\psi_j\right)\left\{\mathcal{E}\left(\mathbf{C}\left(\psi\right),\psi\right) - \mathcal{E}_{N-1}\left(\mathbf{C}\left(\psi\right),\psi,\psi_j\right)\right\}$$
$$\equiv \Xi_j\left(\psi_j\right) I\left(\psi_j\right); \qquad 1 \leq j \leq 2s$$

Where (a)

- $\mathcal{E}\left(\mathbf{C}\left(\psi\right),\psi\right)$ is the optimized N-electron state energy
- $\mathcal{E}_{N-1}\left(\mathbf{C}\left(\psi\right),\psi,\psi_j\right)$ is the energy of the (unrelaxed) N-1 electron state with the GSO $\left|\psi_j\right\rangle$ removed

- $I\left(\psi_j\right)$ is the ionization energy of an electron that leaves in a state $\left|\psi_j\right\rangle$
- $\Xi_j\left(\psi_j\right)$ is the occupation of the state $\left|\psi_j\right\rangle$

and (b)

the N-electron energy can be expressed as

$$\mathcal{E}\left(\mathbf{C}\left(\psi\right),\psi\right)=\frac{1}{2}\left\{\mathrm{Tr}\left\{F\left(\mathbf{C}\left(\psi\right),\psi\right)\right\}+\mathcal{E}_{1}\left(\mathbf{C}\left(\psi\right),\psi\right)\right\}$$

where the one electron energy is given by

$$\mathcal{E}_{1}\left(\mathbf{C}\left(\psi\right),\psi\right)=\sum_{1\leq j\leq 2s}D^{1}\left(\mathbf{C}\left(\psi\right)\right)_{jk}\left\langle \psi_{k}\right|h_{1}\psi_{j}\rangle$$

Using the invariance of the N-electron state to the combined transformation of the CI coefficients and GSO's we can express this in terms of

- GSO's $\{|\phi_j\rangle | 1 \leq j \leq 2s\}$ **that diagonalize the FORDO** (i.e. GNSO's) giving

$$\mathcal{E}_1(\mathbf{C}(\psi), \psi) = \sum_{1 \leq j \leq 2s} N_j \langle \varphi_j | h_1 \varphi_j \rangle$$

Where $\{ N_j | ; 1 \leq j \leq 2s \}$ are the occupation numbers of the FORDO

Thus the N-electron energy can be expressed as

$$\mathcal{E}\left(\mathbf{C}\left(\psi\right), \psi\right) = \frac{1}{2} \sum_{1 \leq j \leq 2s} N_j \kappa\left(\varphi_j\right)$$

where

$$\kappa\left(\varphi_j\right) = I\left(\varphi_j\right) + h_1\left(\varphi_j\right)$$

and

$$h_1\left(\varphi_j\right) = \sum_{1 \le j \le 2s} \left\langle \varphi_j \middle| h_1 \varphi_j \right\rangle$$

The Generalized Fock operator is not in general diagonal in the GNSO basis but we can consider

• GSO's $\{|\varsigma_j\rangle| 1 \leq j \leq 2s\}$ that **diagonalize the generalized Fock operator** and observe that

$$\varepsilon_j = \Xi_j(\varsigma_j) I(\varsigma_j) \qquad 1 \leq j \leq 2s$$

where the eigenvalues of the Fock operator are $\{\varepsilon_j| 1 \leq j \leq 2s\}$ thus giving

$$\mathrm{Tr}\{F(\mathbf{C}(\psi), \psi)\} = \sum_{1 \leq j \leq 2s} \varepsilon_j$$

Thus

the N-electron energy can be written in terms ionization energies, one particle kinetic energies and one particle external potentials,

(This corresponds to the energy expression obtained from the contour integration of the one electron Greens function)

but

in general it is not determined by one electron properties as one needs the N-electron CI coefficients to determine

$$\{ I(\varphi_j) | \, 1 \leq j \leq 2s \}$$

However

An N-electron AGP state is determined by a set of unnormalized CGSO's $\{\,|\psi_j\rangle|\,1 \leq j \leq 2s\}$

where $\langle\psi_j|\,\psi_k\rangle = n_j\delta_{jk}$

that determine $I\,(\psi_j)$ and hence $\kappa\,(\psi_j)$

and the optimized AGP energy can be expressed entirely in terms of one electron quantities as

$$\mathcal{E}\left(g^{\frac{N}{2}}\left(\psi\right)\right)=\frac{1}{2}\sum_{1\leq j\leq 2s}N\left(\frac{\psi_j}{\sqrt{n_j}}\right)\kappa\left(\frac{\psi_j}{\sqrt{n_j}}\right)$$

Observe that the FORDO is diagonal in the basis

$$\left\{\left|\frac{\psi_j}{\sqrt{n_j}}\right\rangle\middle|\,1\leq j\leq 2s\right\}$$

but the generalized Fock operator is not

Thus we have constructed correlated one electron theory that can be explicitly formulated in terms GSO's and one electron expectation values

The AGP state has appeared in many guises

- Fractional Quantum Hall Effect (FCHE)
  - Pfaffian wavefunctions
  - Composite fermions
- Superconductivity
  - Number projected BCS states
- Random Phase Approximation (RPA)
  - Most consistent ground state of the
- Polarization Propagator
- Ising model

Future Directions

- Implement Optimization Scheme
- Strongly correlated fermion systems
- Quantum dots