GCM for molecules

sdb, ga, pb, at?, dvn?

October 16, 2018

1 in a nut shell

The idea is to do a Generator Coordinate Method (GCM) [1, 2] for molecular systems with the total spin S as the generator coordinate. It is an alternative view on the Holomorphic Hartree-Fock theory by Hugh Burton and Alex Thom in which a non-orthogonal Configuration Interaction (no-CI) is constructed from a basis set consisting of the restricted and unrestricted Hartree-Fock solution (RHF and UHF respectively) [3]. The difference between RHF and UHF is that RHF takes the same set of orbitals for α and β electrons, and therefore imposes good spin tensorial properties $\langle S_z \rangle = \langle \vec{S} \cdot \vec{S} \rangle = 0$, whereas UHF breaks total spin symmetry by allowing for different spatial orbitals for α and β electrons. This suggests[1] that S may be a good generator coordinate.

2 gcm

Assume we have a manifold of wavefunctions $|\psi(a)\rangle$ in some (continuous) variable or parameter a (the generator coordinate). Then, one can build a *correlated* wavefunction[2] by making a (continuous) linear combination over the coordinate a [2]

$$|\Psi\rangle = \int da f(a) |\psi(a)\rangle, \tag{1}$$

with $f(a)$ the so-called weight function. The energy functional is then given by

$$E[f] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{2}$$

which upon variation $\frac{\delta}{\delta f(b)^*}$ yields

$$\int db \langle \psi(a) | H | \psi(b) \rangle f(b) = E \int db \langle \psi(a) | \psi(b) \rangle f(b) \tag{3}$$

This manifold of equations is known as the Hill-Wheeler (HW) equations in the GCM [2]. By defining the Hamiltonian and overlap kernels

$$H(a,b) := \langle \psi(a) | H | \psi(b) \rangle, \quad O(a,b) := \langle \psi(a) | \psi(b) \rangle \tag{4}$$

[1] I have no hard proof, only fingerspitzengefühl

[2] bad nomenclature, it is more of an LCAO, but you can *feel* the correlations

the notation can be considerably compressed

$$\int dbH(a,b)f(b) = E\int dbO(a,b)f(b). \tag{5}$$

To avoid confusion with the spin quantum number, the overlap will be denoted with O. Until now, everything has been left as unspecified as possible, most in particular the generator coordinate a and the associated wavefunction $|\psi(a)\rangle$. A sensible choice of $|\psi(a)\rangle$ is to use a manifold of Slater Determinants (SD) coming from a set of constrained HF calculation with a constraint on the expectation value of some well-chosen operator A. This can be achieved with a Lagrange multiplier on the Hamiltonian in the HF equations

$$\{|\psi(a)\rangle = |\mathrm{SD}\rangle; \delta\langle \mathrm{SD}|H - \lambda(A-a)|\mathrm{SD}\rangle = 0\}. \tag{6}$$

The particular choice of HF calculation (restricted, unrestricted or generalized) will be discussed later.

The Hill-Wheeler equations (5) are defined on a continuous manifold. Obviously, this is not possible to attain in a numerical computation, so one usually discretizes the integral [2].

$$\sum_b H(a,b)f(b) = E\sum_b O(a,b)f(b). \tag{7}$$

So, the discretized Hill-Wheeler equations reduce to a generalized eigenvalue problem, equivalent to what is obtained in no-CI theory. The non-orthogonality arises from the overlap kernel $O(a,b)$, which reflects the non-orthogonality of the different HF solutions at different values of a.

3 Hamiltonian

In second quantization, the most general Hamiltonian is given by

$$H = \sum_{\alpha\beta} t_{\alpha\beta}a^\dagger_\alpha a_\beta + \tfrac{1}{4}\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma, \tag{8}$$

with the normalized antisymmetric matrix elements given by

$$t_{\alpha\beta} = \langle\alpha|T+W|\beta\rangle \tag{9}$$

$$V_{\alpha\beta\gamma\delta} = \langle\alpha\beta|V|\gamma\delta\rangle - \langle\alpha\beta|V|\delta\gamma\rangle \tag{10}$$

Note that Greek indices ($\alpha\beta\gamma\delta$) denote the *full* set of single-particle quantum numbers. Typically, they comprise the *spin* and *spatial* part of the so-called spin orbitals, wich are denoted by

$$\alpha = \begin{cases} a & \text{if spin up} \\ \bar{a} & \text{if spin down} \end{cases} \tag{11}$$

consistent with the notation used further on (**??**).

For the present set of notes, we will assume a spin-independent interaction, as is the case for the non-relativistic Coulomb Hamiltonian [3] Because of the spin symmetry, most of the 2-body matrix elements vanish

[3]Note that it is technically not impossible to treat spin-dependent interactions, such as spin-orbit interactions. It is not clear though (for me, that is) if one will *gain* much from using spin as generator coordinator when it is not a symmetry in the original Hamiltonian.

	cd	$c\bar{d}$	$\bar{c}d$	$\bar{c}\bar{d}$
ab	$\langle ab\|V\|cd\rangle - \langle ab\|V\|dc\rangle$	0	0	0
$a\bar{b}$	0	$\langle ab\|V\|cd\rangle$	$-\langle ab\|V\|dc\rangle$	0
$\bar{a}b$	0	$-\langle ab\|V\|dc\rangle$	$\langle ab\|V\|cd\rangle$	0
$\bar{a}\bar{b}$	0	0	0	$\langle ab\|V\|cd\rangle - \langle ab\|V\|dc\rangle$

So, the Hamiltonian can be written as follows

$$H = \sum_{ab=1}^{L} \langle a|h_0|b\rangle [a_a^\dagger a_b + a_{\bar{a}}^\dagger a_{\bar{b}}] + \frac{1}{2} \sum_{abcd} \langle ab|V|cd\rangle [a_a^\dagger a_b^\dagger a_d a_c \tag{12}$$

$$+ a_{\bar{a}}^\dagger a_b^\dagger a_d a_{\bar{c}} + a_a^\dagger a_{\bar{b}}^\dagger a_{\bar{d}} a_c + a_{\bar{a}}^\dagger a_{\bar{b}}^\dagger a_{\bar{d}} a_{\bar{c}}]. \tag{13}$$

Again, the spatial orbitals are denoted by Latin indices and the bar indicates the spin component. The matrix elements $\langle a|h_0|b\rangle$ and $\langle ab|V|cd\rangle$ are given by the conventional

$$\langle a|h_0|b\rangle = \int d\vec{r} \phi_a^*(\vec{r})[T + W(\vec{r})]\phi_b(\vec{r}) \tag{14}$$

$$\langle ab|V|cd\rangle = \int d\vec{r}_1 d\vec{r}_2 \phi_a^*(\vec{r}_1)\phi_b^*(\vec{r}_2)V(\vec{r}_1, \vec{r}_2)\phi_c(\vec{r}_1)\phi_d(\vec{r}_2) \tag{15}$$

In the case of Hubbard models, which assumes a contact interaction between strongly localized orbitals, there is a further simplification in the matrix elements

$$\langle ab|V|cd\rangle = U_a \delta_{ac} \delta_{bd} \delta_{ab} \tag{16}$$

with U_a the effective Coulomb repulsion felt on site a. The Hamiltonian becomes

$$H = -\sum_{ab=1}^{L} t_{ab}[a_a^\dagger a_b + a_{\bar{a}}^\dagger a_{\bar{b}}] + \sum_a U_a a_{\bar{a}}^\dagger a_{\bar{a}} a_a^\dagger a_a. \tag{17}$$

with the typical definition of the hopping matrix t

$$t_{ab} = -\langle a|h_0|b\rangle. \tag{18}$$

4 spin

The idea is to use the total spin S as the generator coordinate. The operators associated with spin are (within an L-dimensional orthogonal basis set)

$$S^\dagger = \sum_{i=1}^{L} a_i^\dagger a_{\bar{i}}, \quad S = (S^\dagger)^\dagger = \sum_{i=1}^{L} a_{\bar{i}}^\dagger a_i \quad S^0 = \sum_{i=1}^{L} \tfrac{1}{2}(a_i^\dagger a_i - a_{\bar{i}}^\dagger a_{\bar{i}}), \tag{19}$$

in which we have used the $\{i, \bar{i}\}$ notation to denote respectively spin-up and -down electrons in spatial orbital i. In this notation, we can label the orbital specific spin algebras

$$S_i^\dagger = a_i^\dagger a_{\bar{i}}, \quad S_i = (S_i^\dagger)^\dagger = a_{\bar{i}}^\dagger a_i \quad S_i^0 = \tfrac{1}{2}(a_i^\dagger a_i - a_{\bar{i}}^\dagger a_{\bar{i}}), \tag{20}$$

in the sense that it describes the spin-properties of electrons in the ith spatial orbital. The total spin operator is given by

$$\vec{S} \cdot \vec{S} = (S^0)^2 + \tfrac{1}{2}(S^\dagger S + S S^\dagger). \tag{21}$$

which is given explicitly as

$$\vec{S} \cdot \vec{S} = \tfrac{3}{4} \sum_{i=1}^{L} (a_i^\dagger a_i + a_{\bar{i}}^\dagger a_{\bar{i}}) + \sum_{ij=1}^{L} a_i^\dagger a_{\bar{j}}^\dagger a_j a_{\bar{i}} \tag{22}$$

$$+ \sum_{ij=1}^{L} \tfrac{1}{4} [a_i^\dagger a_j^\dagger a_j a_i - a_{\bar{i}}^\dagger a_j^\dagger a_j a_{\bar{i}} - a_i^\dagger a_{\bar{j}}^\dagger a_{\bar{j}} a_i + a_{\bar{i}}^\dagger a_{\bar{j}}^\dagger a_{\bar{j}} a_{\bar{i}}] \tag{23}$$

in the two-particle scattering picture in which the Hamiltonian will be expressed.

4.1 Total spin as a 2-body interaction

It is interesting to note that the total spin operator (23) in 2nd quantization can also be obtained from an interaction picture in which particles interact pairwize via the spin-spin interaction. In 1st quantization, the operator looks like

$$\vec{S} \cdot \vec{S} = \sum_{i=1}^{N} \vec{S}(\sigma_i) \cdot \vec{S}(\sigma_i) + \sum_{i<j} 2\vec{S}(\sigma_i) \cdot \vec{S}(\sigma_j) \tag{24}$$

which is clearly composed of a 1-body operator (first term) and 2-body interaction (second term). Here, the variable σ_i are to be interpreted as the (abstract) spin coordinates of a particle with index i. Note the factor 2 in the 2-body interaction to make it a genuine interaction term. Going to second quantization, the "Hamiltonian" can be written as

$$\vec{S} \cdot \vec{S} = \sum_{\alpha\beta} s_{\alpha\beta} a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} S_{\alpha\beta\gamma\delta} a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \tag{25}$$

with the matrix elements given by the standard (antisymmetrized) expressions

$$s_{\alpha\beta} = \langle \alpha | \vec{S}(\sigma) \cdot \vec{S}(\sigma) | \beta \rangle \tag{26}$$

$$S_{\alpha\beta\gamma\delta} = \langle \alpha\beta | 2\vec{S}(\sigma_1) \cdot \vec{S}(\sigma_2) | \gamma\delta \rangle - \langle \alpha\beta | 2\vec{S}(\sigma_1) \cdot \vec{S}(\sigma_2) | \delta\gamma \rangle. \tag{27}$$

It is necessary to make the distinction between spin-up ($\alpha = a$) and spin-down ($\alpha = \bar{a}$) quantum numbers. The non-zero 1-body matrix elements are given by

$$s_{ab} = \int d\vec{r} d\sigma \phi_a^*(\vec{r}) \chi_\uparrow^*(\sigma) \vec{S}(\sigma) \cdot \vec{S}(\sigma) \phi_b(\vec{r}) \chi_\uparrow(\sigma) = \delta_{ab} \tfrac{3}{4} \tag{28}$$

$$s_{\bar{a}\bar{b}} = \int d\vec{r} d\sigma \phi_a^*(\vec{r}) \chi_\downarrow^*(\sigma) \vec{S}(\sigma) \cdot \vec{S}(\sigma) \phi_b(\vec{r}) \chi_\downarrow(\sigma) = \delta_{ab} \tfrac{3}{4} \tag{29}$$

The non-zero 2-body matrix elements are given by

$$S_{abcd} = \delta_{ac}\delta_{bd} 2\langle\uparrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\uparrow\rangle - \delta_{ad}\delta_{bc} 2\langle\uparrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\uparrow\rangle \tag{30}$$

$$S_{a\bar{b}c\bar{d}} = \delta_{ac}\delta_{bd} 2\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle - \delta_{ad}\delta_{bc} 2\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle \tag{31}$$

$$S_{a\bar{b}\bar{c}d} = \delta_{ac}\delta_{bd} 2\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle - \delta_{ad}\delta_{bc} 2\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle \tag{32}$$

$$S_{\bar{a}bc\bar{d}} = \delta_{ac}\delta_{bd} 2\langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle - \delta_{ad}\delta_{bc} 2\langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle \tag{33}$$

$$S_{\bar{a}b\bar{c}d} = \delta_{ac}\delta_{bd} 2\langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle - \delta_{ad}\delta_{bc} 2\langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle \tag{34}$$

$$S_{\bar{a}\bar{b}\bar{c}\bar{d}} = \delta_{ac}\delta_{bd} 2\langle\downarrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\downarrow\rangle - \delta_{ad}\delta_{bc} 2\langle\downarrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\downarrow\rangle. \tag{35}$$

with the spin part given explicitly by

$$\langle\uparrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\uparrow\rangle = \langle\downarrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\downarrow\rangle = \tfrac{1}{4}, \tag{36}$$

$$\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle = \langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle = -\tfrac{1}{4}, \tag{37}$$

$$\langle\uparrow\downarrow|\vec{S}_1\cdot\vec{S}_2|\downarrow\uparrow\rangle = \langle\downarrow\uparrow|\vec{S}_1\cdot\vec{S}_2|\uparrow\downarrow\rangle = \tfrac{1}{2}, \tag{38}$$

leading to

$$S_{abcd} = S_{\bar{a}\bar{b}\bar{c}\bar{d}} = \tfrac{1}{2}\delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc} \tag{39}$$

$$S_{a\bar{b}\bar{c}d} = S_{\bar{a}bc\bar{d}} = \delta_{ac}\delta_{bd} + \tfrac{1}{2}\delta_{ad}\delta_{bc} \tag{40}$$

$$S_{a\bar{b}c\bar{d}} = S_{\bar{a}b\bar{c}d} = -\tfrac{1}{2}\delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc}. \tag{41}$$

With this, the total spin operator becomes

$$\vec{S}\cdot\vec{S} = \tfrac{3}{4}N + \sum_{ab} a_a^\dagger a_{\bar{b}}^\dagger a_b a_{\bar{a}} \tag{42}$$

$$+ \tfrac{1}{4}\sum_{ab}[a_a^\dagger a_b^\dagger a_b a_a - a_a^\dagger a_{\bar{b}}^\dagger a_{\bar{b}} a_a - a_{\bar{a}}^\dagger a_b^\dagger a_b a_{\bar{a}} + a_{\bar{a}}^\dagger a_{\bar{b}}^\dagger a_{\bar{b}} a_{\bar{a}}] \tag{43}$$

4.2 tensorial properties

The spin operators (20) generate a direct sum of $su(2)$ Lie-algebras $\oplus_{i=1}^{L} su(2)_i$ under commutation

$$[S_i^0, S_j^\dagger] = \delta_{ij} S_i^\dagger, \quad [S_i^0, S_j] = -\delta_{ij} S_i, \quad [S_i^\dagger, S_j] = 2\delta_{ij} S_i^0. \tag{44}$$

As a result, there is an $su(2)$ algebraic structure associated with each spatial orbital (i), independent of the other orbitals. The set of particle creation operators $\{a_i^\dagger, a_{\bar{i}}^\dagger\}$ has good $s = \frac{1}{2}$ spinor properties under this $su(2)_i$, so we can write

$$a_{i,\frac{1}{2}}^\dagger = a_i^\dagger, \quad a_{i,-\frac{1}{2}}^\dagger = a_{\bar{i}}^\dagger. \tag{45}$$

For the annihilation operators to have good $s = \frac{1}{2}$ character, we need to redefine them as hole operators (note the $-$)

$$\tilde{a}_{i,\frac{1}{2}} = a_{\bar{i}}, \quad \tilde{a}_{i,-\frac{1}{2}} = -a_i. \tag{46}$$

This redefinition allows for good tensorial properties under recoupling (see later). For instance, the number operator can be rewritten as

$$n_i = -\sqrt{2}[a_i \tilde{a}_i]_0^{(0)} = \sum_{m_1=\pm\frac{1}{2}} \sum_{m_2=\pm\frac{1}{2}} \langle \tfrac{1}{2} m_1 \tfrac{1}{2} m_2 | 00\rangle a_{i,m_1}^\dagger \tilde{a}_{i,m_2} \tag{47}$$

5 constrained Hartree-Fock

We will perform a Hartree-Fock calculation on the constrained Hamiltonian

$$\mathcal{H} = H - \lambda(\vec{S}\cdot\vec{S} - S(S+1)) - \mu(S_z - M) \tag{48}$$

5.1 recap on HF

Here, we assume that we are dealing with an orthogonal basis. This is not necessarily the case, for which we will have to deal with Roothaan equations instead of Hartree-Fock equations (`tbd`). Hartree-Fock theory pursues the variational minimum of a many-body system with a Slater determinant trial state. Arguably the best way to understand HF theory in second quantization is via the Wick theorem [4, 2]. Take the most general Hamiltonian (8)

$$H = \sum_{\alpha\beta} t_{\alpha\beta} a^\dagger_\alpha a_\beta + \frac{1}{4}\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma, \tag{49}$$

with the (normalized antisymmetric) standard expressions for the matrix elements

$$t_{\alpha\beta} = \langle\alpha|\hat{T} + W|\beta\rangle, \qquad V_{\alpha\beta\gamma\delta} = \langle\alpha\beta|\hat{V}|\gamma\delta\rangle - \langle\alpha\beta|\hat{V}|\delta\gamma\rangle. \tag{50}$$

Because of the Wick theorem, the 2dm in the HF vaccuum state reduces to an antisymmetric product of (idempotent) 1dms

$$\langle a^\dagger_\alpha a^\dagger_\beta a_\gamma a_\delta\rangle = \langle a^\dagger_\alpha a_\delta\rangle\langle a^\dagger_\beta a_\gamma\rangle - \langle a^\dagger_\alpha a_\gamma\rangle\langle a^\dagger_\beta a_\delta\rangle \tag{51}$$

The HF energy is then given by

$$E_{\mathrm{HF}} = \sum_{\alpha\beta} t_{\alpha\beta}\rho_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} \rho_{\alpha\gamma} V_{\alpha\beta\gamma\delta}\rho_{\beta\delta}, \tag{52}$$

with the 1dm renamed as

$$\rho_{\alpha\beta} = \langle a^\dagger_\alpha a_\beta\rangle. \tag{53}$$

Minimization of this energy expression with a constraint on the idempotency of the 1dm ($\rho^2 = \rho$) leads to the definition of the Fock matrix

$$F_{\mu\nu} = t_{\mu\nu} + \sum_{\alpha\gamma} V_{\alpha\mu\gamma\nu}\rho_{\alpha\gamma}, \tag{54}$$

and the associated Fock operator

$$\hat{F} = \sum_{\mu\nu} F_{\mu\nu} a^\dagger_\mu a_\nu. \tag{55}$$

Note that the dimension of the Fock matrix is equal to the number of orbitals involved. The crucial point is now that the 1dm commutes with the Fock *matrix*

$$[F, \rho] = 0. \tag{56}$$

As a result, the HF vaccuum is obtained by the particular single-particle rotation that diagonalises the Fock operator and 1dm simultaneously

$$F_{\mu\nu} = t_{\mu\nu} + \sum_{\alpha\gamma} V_{\alpha\mu\gamma\nu}\rho_{\alpha\gamma} = \epsilon_\mu \delta_{\mu\nu}. \tag{57}$$

Because ρ depends on the state itself, it must be solved self consistently. Furthermore, the idempotency of the 1dm must still be guaranteed

$$\rho^2 = \rho, \tag{58}$$

as well as the trace condition

$$\mathrm{Tr}(\rho) = N \tag{59}$$

with N the number of particles.

5.2 hf for spin symmetric systems

We still assume orthogonal wave functions. The Fock matrix breaks down into spin-dependent parts

$$F_{bd} = \langle b|h_0|d\rangle + \sum_{ac}[\langle ab|V|cd\rangle(\rho_{ac} + \rho_{\bar{a}\bar{c}}) - \langle ab|V|dc\rangle\rho_{ac}], \tag{60}$$

$$F_{b\bar{d}} = -\sum_{ac}\langle ab|V|dc\rangle\rho_{\bar{a}c}, \tag{61}$$

$$F_{\bar{b}d} = -\sum_{ac}\langle ab|V|dc\rangle\rho_{a\bar{c}}, \tag{62}$$

$$F_{\bar{b}\bar{d}} = \langle b|h_0|d\rangle + \sum_{ac}[\langle ab|V|cd\rangle(\rho_{\bar{a}\bar{c}} + \rho_{ac}) - \langle ab|V|dc\rangle\rho_{\bar{a}\bar{c}}]. \tag{63}$$

Note that these relations simplify significantly in case of the Hubbard model (17).

$$F_{bd} = -t_{bd} + U_b\delta_{bd}\rho_{\bar{b}\bar{b}}, \tag{64}$$

$$F_{b\bar{d}} = -U_b\delta_{bd}\rho_{\bar{b}d}, \tag{65}$$

$$F_{\bar{b}d} = -U_b\delta_{bd}\rho_{b\bar{d}}, \tag{66}$$

$$F_{\bar{b}\bar{d}} = -t_{bd} + U_b\delta_{bd}\rho_{bd}. \tag{67}$$

5.3 Spin constraint

Adding the spin constraint can be regarded as The

6 no-CI

Obviously, SDs resulting from different constraints on A will be non-orthogonal. Assume we have a set of L orthogonal orbitals that will serve as a reference set

$$\{a_i, a_j^\dagger\} = \delta_{ij}, \quad \forall i,j = 1,\ldots,L. \tag{68}$$

Each SD can be expressed as a product state of single-particle operators that are connected to the reference set via a unitary transformation

$$b_i(\alpha) = \sum_{k=1}^{L} U(\alpha)_{ik} a_k. \tag{69}$$

The variable α distinguishes between different SD states, which in our case would come from different values of the constraint. The non-orthogonality is a direct consequence of the non-orthogonality of the unitary matrices

$$\{b_i(\beta), b_j^\dagger(\alpha)\} = (U(\beta)U^\dagger(\alpha))_{ij}. \tag{70}$$

Note that the previous expression is only the kronecker-δ whenever $\beta = \alpha$

$$\{b_i(\alpha), b_j^\dagger(\alpha)\} = (U(\alpha)U^\dagger(\alpha))_{ij} = (1)_{ij} = \delta_{ij}. \tag{71}$$

Another aspect worth noting is that the generalized creation/annihilation operators (69) still anticommute independent of the variable α

$$\{b_i(\beta), b_j(\alpha)\} = 0 \quad \forall \alpha, \beta. \tag{72}$$

Within a no-CI calculation framework, we need to know the overlap of two SDs with different α. An N-particle SD can be represented by means of a set of N integers $\{i\} = \{i_1, i_2, \ldots, i_N\}$ indicating which fermion creation operators $b_{i_k}^\dagger$ (69) are included in the SD

$$|\mathrm{SD}(\alpha, \{i\})\rangle = \prod_{k=1}^{N} b_{i_k}^\dagger(\alpha)|\theta\rangle. \qquad (1 \leq i_k \leq L, \forall k = 1, \ldots, N) \tag{73}$$

Making use of Wick's theorem [5], one can realise that the overlap between two non-orthogonal SDs (that are internally orthogonal) is given by

$$\langle \mathrm{SD}(\alpha, \{i\})|\mathrm{SD}(\beta, \{j\})\rangle = \sum_{\sigma \in S_n} (-)^\sigma \prod_{l=1}^{N} \langle\theta| b_{i_{\sigma(l)}}(\alpha) b_{j_l}^\dagger(\beta)|\theta\rangle, \tag{74}$$

which is the formula for $\det M(\alpha, \beta)$ with

$$M_{kl}(\alpha, \beta) = \langle\theta| b_{i_k}(\alpha) b_{j_l}^\dagger(\beta)|\theta\rangle = (U(\alpha)U^\dagger(\beta))_{i_k j_l}. \tag{75}$$

Note that whenever $\alpha = \beta$, $U^\dagger(\alpha)U(\alpha) = 1$, so the matrix M has only non-zero rows/columns when $\{i\} = \{j\}$ up to a permutation. The sign of $\det M$ will be equal to the sign of the permutation.

7 examples

7.1 2-site hubbard

The Hamiltonian is given by

$$H = -t \sum_{\sigma=\downarrow,\uparrow} [a_{L\sigma}^\dagger a_{R\sigma} + a_{R\sigma}^\dagger a_{L\sigma}] + U[n_{L\uparrow} n_{L\downarrow} + n_{R\uparrow} n_{R\downarrow}] \tag{76}$$

with $\{L, R\}$ denoting the left or right site of the model (parity is a trivial symmetry), and t and U the typical hopping and on-site repulsion parameters respectively. We will only consider the half-filled space ($N = 2$)

7.1.1 fCI

The fCI space is built from the Fock states

$$|1\rangle = a^\dagger_{L\uparrow}a^\dagger_{L\downarrow}|\theta\rangle, \quad |2\rangle = a^\dagger_{R\uparrow}a^\dagger_{R\downarrow}|\theta\rangle, \quad |3\rangle = a^\dagger_{L\uparrow}a^\dagger_{R\downarrow}|\theta\rangle, \quad |4\rangle = a^\dagger_{R\uparrow}a^\dagger_{L\downarrow}|\theta\rangle,$$
$$|5\rangle = a^\dagger_{L\uparrow}a^\dagger_{R\uparrow}|\theta\rangle, \quad |6\rangle = a^\dagger_{L\downarrow}a^\dagger_{R\downarrow}|\theta\rangle. \tag{77}$$

The first four states are $M = 0$ states, whereas $|5\rangle$ and $|6\rangle$ are $M = 1$ and $M = -1$ respectively. Because of the spin-projection symmetry, only the $M = 0$ space is non-trivial. The action of the Hamiltonian gives rise to the following relations

$$H|1\rangle = U|1\rangle - t|3\rangle - t|4\rangle, \tag{78}$$
$$H|2\rangle = U|2\rangle - t|3\rangle - t|4\rangle, \tag{79}$$
$$H|3\rangle = -t|1\rangle - t|2\rangle, \tag{80}$$
$$H|4\rangle = -t|1\rangle - t|2\rangle, \tag{81}$$

from which we can find the four eigenvalues with their eigenstates

- $\lambda = 0$: The constant-energy state is given by

  $$|\lambda = 0\rangle = \tfrac{1}{\sqrt{2}}(|3\rangle - |4\rangle) = \tfrac{1}{\sqrt{2}}(a^\dagger_{L\uparrow}a^\dagger_{R\downarrow} + a^\dagger_{L\downarrow}a^\dagger_{R\uparrow})|\theta\rangle \tag{82}$$

  which is the $M = 0$ state of the $S = 1$ triplet.

- $\lambda = U$: This state (polarized?) is given by

  $$|\lambda = U\rangle = \tfrac{1}{\sqrt{2}}(|1\rangle - |2\rangle) = \tfrac{1}{\sqrt{2}}(a^\dagger_{L\uparrow}a^\dagger_{L\downarrow} - a^\dagger_{R\uparrow}a^\dagger_{R\downarrow})|\theta\rangle \tag{83}$$

  which is a pure $S = 0$ closed singlet configuration (in terms of the LR orbital scheme)

- $\lambda_\pm = \frac{1}{2}U \pm \sqrt{(\frac{U}{2})^2 + (2t)^2}$: the interacting states are given by

  $$|\lambda_\pm\rangle = \cos\theta_\pm \tfrac{1}{\sqrt{2}}(|1\rangle + |2\rangle) + \sin\theta_\pm \tfrac{1}{\sqrt{2}}(|3\rangle + |4\rangle), \tag{84}$$

  with

  $$\tan\theta_\pm = \tfrac{U}{4t} \mp \sqrt{\left(\tfrac{U}{4t}\right)^2 + 1} \tag{85}$$

  Note that $\tan\theta_+ \tan\theta_- = -1$, such that $\theta_+ - \theta_- = \frac{\pi}{2}$, pointing out that $|\lambda_\pm\rangle$ are indeed mutually orthogonal. The $|\lambda_-\rangle$ state is typically the ground state.

The energy spectra associated to the four states are plotted in Figure 1 as a function of the parameter ξ with $t = 1 - \xi$ and $U = \xi$. As a result, we have a transition from the completely delocalized regime ($\xi = 0$ or $U = 0$) to the "infinite separation" regime ($\xi = 1$ or $t = 0$).

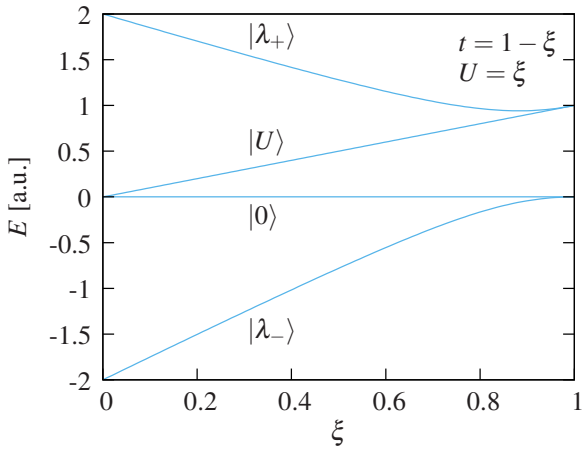

Figure 1: Spectrum of the 2-site Hubbard model (76) as a function of the parameter ξ with $(t, U) = (1 - \xi, \xi)$. The states are labeled by their energy.

7.1.2 spin

The total spin $su(2)$ algebra is spanned by

$$S^\dagger = S_L^\dagger + S_R^\dagger, \quad S = S_L + S_R, \quad S^0 = S_L^0 + S_R^0, \tag{86}$$

with the orbital spin operators given by

$$S_R^\dagger = a_{R\uparrow}^\dagger a_{R\downarrow}, \quad S_R = a_{R\downarrow}^\dagger a_{R\uparrow}, \quad S_R^0 = \tfrac{1}{2}(a_{R\uparrow}^\dagger a_{R_\uparrow} - a_{R\downarrow}^\dagger a_{R_\downarrow}) \tag{87}$$

$$S_L^\dagger = a_{L\uparrow}^\dagger a_{L\downarrow}, \quad S_L = a_{L\downarrow}^\dagger a_{L\uparrow}, \quad S_L^0 = \tfrac{1}{2}(a_{L\uparrow}^\dagger a_{L_\uparrow} - a_{L\downarrow}^\dagger a_{L_\downarrow}). \tag{88}$$

As a result, the total spin operator is given explicitly by

$$\vec{S} \cdot \vec{S} = \vec{S}_L \cdot \vec{S}_L + 2\vec{S}_L \cdot \vec{S}_R + \vec{S}_R \cdot \vec{S}_R, \tag{89}$$

$$= \tfrac{3}{4} + \tfrac{3}{4} - a_{L\uparrow}^\dagger a_{R\downarrow}^\dagger a_{L\downarrow} a_{R\uparrow} - a_{R\uparrow}^\dagger a_{L\downarrow}^\dagger a_{R\downarrow} a_{L\uparrow} \tag{90}$$

$$+ \tfrac{1}{2}(a_{L\uparrow}^\dagger a_{L_\uparrow} - a_{L\downarrow}^\dagger a_{L_\downarrow})(a_{R\uparrow}^\dagger a_{R_\uparrow} - a_{R\downarrow}^\dagger a_{R_\downarrow}) \tag{91}$$

The action on the basis states is given by

$$\vec{S} \cdot \vec{S}|1\rangle = 0, \tag{92}$$

$$\vec{S} \cdot \vec{S}|2\rangle = 0, \tag{93}$$

$$\vec{S} \cdot \vec{S}|3\rangle = |3\rangle - |4\rangle, \tag{94}$$

$$\vec{S} \cdot \vec{S}|4\rangle = -|3\rangle + |4\rangle. \tag{95}$$

leading further to the conclusion that $|\lambda = 0\rangle$ is indeed a $S = 1$ state, whereas the others are all $S = 0$ states.

7.1.3 unrestricted HF

We will first consider unrestricted HF because of its conceptual simplicity. It describes a Slater Determinant $|\mathrm{SD}\rangle$ with the $\uparrow$ and $\downarrow$ components differing

$$|\mathrm{SD}\rangle = (\cos\alpha a^\dagger_{L\uparrow} + \sin\alpha a^\dagger_{R\uparrow})(\cos\beta a^\dagger_{L\downarrow} + \sin\beta a^\dagger_{R\downarrow})|\theta\rangle \tag{96}$$

$$= \cos\alpha\cos\beta|1\rangle + \sin\alpha\sin\beta|2\rangle + \cos\alpha\sin\beta|3\rangle + \sin\alpha\cos\beta|4\rangle \tag{97}$$

Note that we recover restricted Hartree-Fock (RHF) when we choose or get $\alpha = \beta$. The expectation value of the Hamiltonian (76) wrt this (normalized) SD is

$$E[\alpha,\beta] = \langle \mathrm{SD}|H|\mathrm{SD}\rangle \tag{98}$$

$$= \tfrac{1}{2}U[1 + \cos 2\alpha\cos 2\beta] - t[\sin 2\alpha + \sin 2\beta]$$

The stability equations, or HF equations are given by

$$\frac{\partial E}{\partial \alpha} = -U\cos 2\beta\sin 2\alpha - 2t\cos 2\alpha = 0 \tag{99}$$

$$\frac{\partial E}{\partial \beta} = -U\cos 2\alpha\sin 2\beta - 2t\cos 2\beta = 0 \tag{100}$$

Among the many solutions, the following are of particular inerest

- The trivial solution $\alpha = \beta = \frac{\pi}{4}$ ($\cos 2\alpha = \cos 2\beta = 0$) is the Restricted Hartree-Fock solution

  $$|\mathrm{RHF}\rangle = \tfrac{1}{2}(a^\dagger_{L\uparrow} + a^\dagger_{R\uparrow})(a^\dagger_{L\downarrow} + a^\dagger_{R\downarrow})|\theta\rangle \tag{101}$$

  The energy associated to this state is

  $$E[\tfrac{\pi}{4},\tfrac{\pi}{4}] = \tfrac{1}{2}U - 2t, \tag{102}$$

  which is exact at the $U = 0$ limit.

- The solution $\sin 2\alpha = \sin 2\beta = \frac{2t}{U}$ is not trivial, because α and β are not necessarily equal. Indeed, the stability equations say that $\cos 2\alpha + \cos 2\beta = 0$, leading to $\alpha + \beta = \frac{\pi}{2}$. This is the UHF solution. Note that this solution is only possible whenever

  $$\tfrac{2t}{U} \leq 1, \tag{103}$$

  because of the trigonometric nature of the solution $\sin 2\alpha = \sin 2\beta = \frac{2t}{U}$. The point for which $\frac{2t}{U} = 1$ corresponds to the so called Coulson-Fisher point of UHF. For values of U larger than $2t$, it is energetically favourable for the system to (artificially) break spin symmetry, leading to a UHF energy that is lower than the RHF equivalent. The energy associated to this solution is given by

  $$E[\alpha_{\mathrm{uhf}}, \tfrac{\pi}{2} - \alpha_{\mathrm{uhf}}] = -\frac{1}{2}\frac{(2t)^2}{U} \tag{104}$$

  with $\alpha_{\mathrm{uhf}} = \frac{1}{2}\arccos\sqrt{1 - (\frac{2t}{U})^2} > 0$.

The RHF and UHF energies are given in Figure 2 in comparison with the exact fCI ground-state energy from $|\lambda_-\rangle$. In the parametrisation of Figure 1, the Coulson Fisher point happens at $\xi = \frac{2}{3}$, where there is a bifurcation between UHF and RHF.

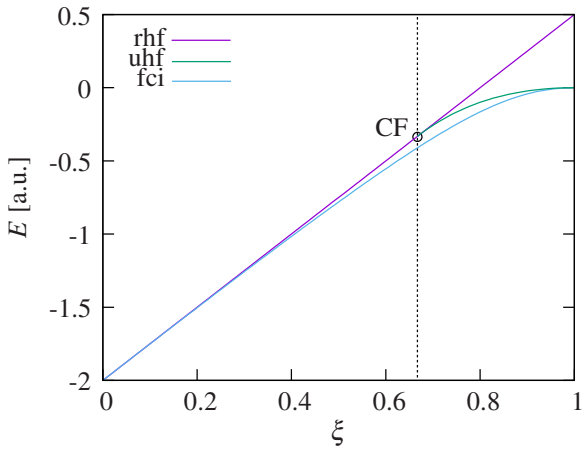

Figure 2: RHF (102) and UHF (104) energies for the 2-site hubbard system, compared to the energy of the fci ground state $|\lambda_-\rangle$. The Coulson Fisher point (CF) is denoted by means of a dotted line at $\xi = \frac{2}{3}$.

7.1.4 constrained HF

We will now move to a constrained version of HF with a constraint on the total spin. Before doing this, it is insightful to investigate the spin contamination in the R/UHF wavefunction. The expectation value of the total spin operator is given by

$$\langle \mathrm{SD}|\vec{S}\cdot\vec{S}|\mathrm{SD}\rangle = \sin^2(\alpha-\beta), \tag{105}$$

which leads to

$$\langle \mathrm{RHF}|\vec{S}\cdot\vec{S}|\mathrm{RHF}\rangle = 0. \tag{106}$$

$$\langle \mathrm{UHF}|\vec{S}\cdot\vec{S}|\mathrm{UHF}\rangle = 1-\left(\tfrac{2t}{U}\right)^2, \tag{107}$$

respectively. One can indeed see from Figure 3 how the spin bifurcates as well at the CF point. It is worth noting that the maximum spin reached (at $\xi = 1$) corresponds to $\langle \vec{S}\cdot\vec{S}\rangle = 1$, which leads to $S = \frac{\sqrt{5}-1}{2} \neq 1$. The reason for this is that UHF is unable to describe a pure triplet state ($S = 1$). More generally, UHF will *not* be able to describe fully polarized spin states for N particle systems ($S = \frac{1}{2}N$). If this is desired, one would have to resort to *generalized* HF (GHF).

Spin-constrained Hartree-Fock theory can now be phrased as the minimization of the Lagrangian

$$\mathcal{L} = H - \lambda[\vec{S}\cdot\vec{S} - S(S+1)] \tag{108}$$

with respect to an unrestricted SD. The Lagrange multiplier λ puts the constraint on the spin. The energy surface is given by

$$E[\alpha,\beta;\lambda] = \tfrac{1}{2}U[1+\cos 2\alpha\cos 2\beta] - t[\sin 2\alpha + \sin 2\beta] \tag{109}$$

$$- \lambda[\sin^2(\alpha-\beta) - S(S+1)], \tag{110}$$

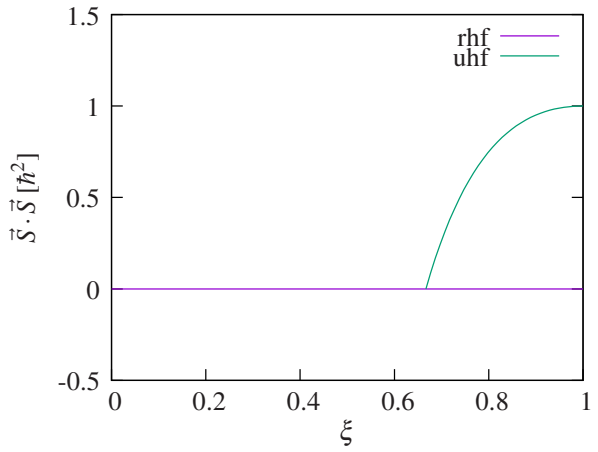

Figure 3: Expectation values of the spin operator $\vec{S}\cdot\vec{S}$ for RHF and UHF ((106) and (107) respectively) for the 2-site hubbard model as a function of ξ (defined in Figure 1.

and the stability equations are now generalized to

$$\frac{\partial E}{\partial \alpha} = -U\cos 2\beta \sin 2\alpha - 2t\cos 2\alpha - \lambda \sin(2(\alpha-\beta)) = 0 \tag{111}$$

$$\frac{\partial E}{\partial \beta} = -U\cos 2\alpha \sin 2\beta - 2t\cos 2\beta + \lambda \sin(2(\alpha-\beta)) = 0 \tag{112}$$

$$\frac{\partial E}{\partial \lambda} = -\sin^2(\alpha-\beta) + S(S+1) = 0. \tag{113}$$

This set of solutions does not lead to solutions in closed form, so we have to resort to numerics. However, one can easily deduce a few generic features.

- The spin contamination is completely imposed by the constraint, which is reflected by eq. (113). As soon as $S \neq 0$, the SD immediately breaks spin symmetry to fulfill the constraint. This a desired feature.
- The $S \equiv 0$ limit coincides with RHF.
- The $S(S+1) = 1 - (\frac{2t}{U})^2$ solution coincides with UHF with $\lambda = 0$.
- Numerical evidence shows that $S \to \frac{\sqrt{5}-1}{2}$ leads to[4] $\alpha \to 0$ and $\beta \to \frac{\pi}{2}$ with $\lambda \to \infty$. The energy of this solution is $E[0, \frac{\pi}{2}, \infty] = 0$ for all ξ.

The constrained energy surfaces for different values of $S = 0, \ldots, \frac{31}{32}S_{\max}$ are plotted in Figure 4 All these surfaces appear to be straight lines[5], with the $S = 0$ coinciding with RHF, and all other surfaces tangent to the UHF solution. A different way of plotting these results is to put $E[\alpha(S), \beta(S), S]$ as a function of S. This is done in Figure for different values of ξ. It is clear from this figure that for small values of ξ (large hopping), the minimum energy is found around

[4] tbd: prove this with perturbation theory!
[5] although I think they are not straight lines for generic cases

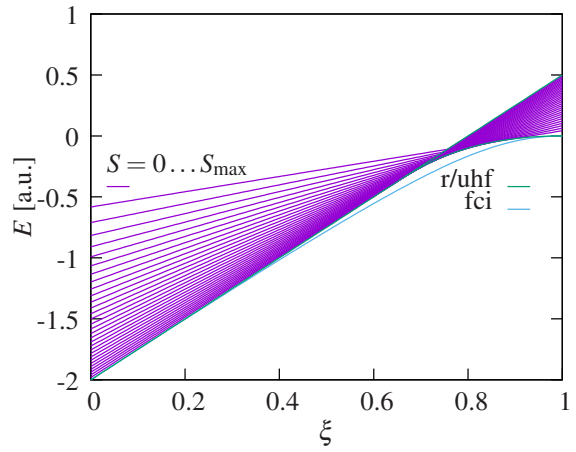

Figure 4: Constrained Hartree-Fock energies for different values of ξ. The RHF and UHF potential energy surfaces are also given.

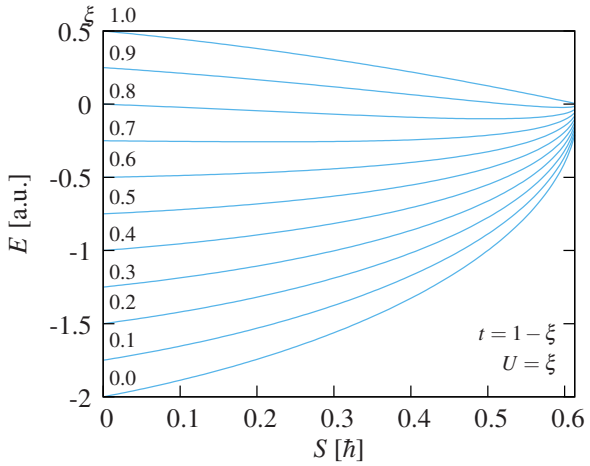

Figure 5: Potential energy surfaces for the 2-site hubbard Hamiltonian from constrained Hartree-Fock as a function of S

$S = 0$, whereas an $S \neq 0$ solution is prefered once the CF point is crossed. This is consistent with the idea of a symmetry breaking.

7.1.5 noci

The key idea of the GCM is to employ a noCI with different constrained-HF states as basis states. Call these states $|\mathrm{SD}_i\rangle$, each defining a different set of (α_i, β_j) angles for the up and down-spin part. We now need the Hamiltonian and overlap matrix. The overlap matrix elements are given by

$$O_{ij} = \langle \mathrm{SD}_i | \mathrm{SD}_j \rangle = \cos(\alpha_i - \alpha_j) \cos(\beta_i - \beta_j), \tag{114}$$

and the Hamiltonian matrix elements are

$$H_{ij} = \tfrac{1}{2}U[\cos(\alpha_i + \alpha_j)\cos(\beta_i + \beta_j) + \cos(\alpha_i - \alpha_j)\cos(\beta_i - \beta_j)] \quad (115)$$

$$- t[\cos(\alpha_i - \alpha_j)\sin(\beta_i + \beta_j) + \sin(\alpha_i + \alpha_j)\cos(\beta_i - \beta_j)]. \quad (116)$$

Note that we recover the UHF energy expression $E[\alpha, \beta]$ (104) on the diagonal ($\alpha_i = \alpha_j, \beta_i = \beta_j$), like we should.

Finding the noCI energies E and quantum states $|\psi\rangle$ corresponds to solving the generalized eigenvalue problem

$$H|\psi\rangle = EO|\psi\rangle. \quad (117)$$

For the noci calculation, we can envision a very simple rule. Take $n = \dim[\text{noci}]$ equidistant points in the $S = [0, \ldots, S_{\max}]$ interval, and perform a constrained-HF calculation at these points. Take the resulting $|\text{SD}\rangle$s as input for the noci. The spectrum for $n = 2$ and $n = 3$ are given in Figure 6. Note that the $n = 3$

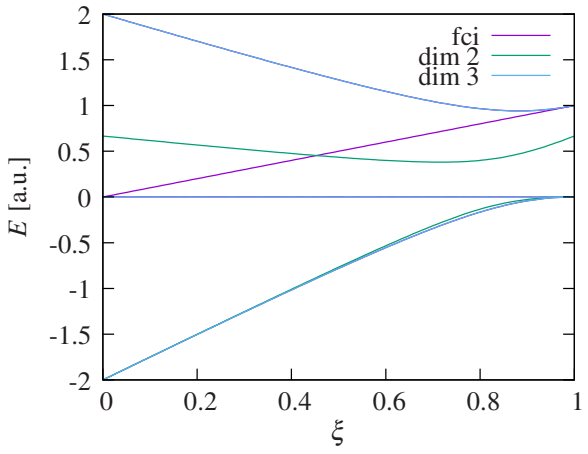

Figure 6: GCM calculations for 2-site hubbard with an equidistant grid in S.. The $n = 3$ results (blue) coincide visually with the fci calculations (purple).

calculations coincide with the $|\lambda_\pm\rangle$ and $|\lambda = 0\rangle$ eigenvalues.

Obviously, there will be more clever ways to construct the noci basis, but that is better addressed in more intricate systems.

References

[1] Reinhard P G and Goeke K 1987 *Rep. Prog. Phys.* **50** 1

[2] Ring P and Schuck P 2004 *The Nuclear Many-Body Problem* 3rd ed (Berlin: Springer)

[3] Burton H G A and Thom A J W 2016 *J. Chem. Theor. Comp.* **12** 167

[4] Rowe D J 1970 *Nuclear Collective Motion* (London: Methuen)

[5] Fetter L and Walecka J D 1971 *Quantum theory of many-particle systems* (New York: McGraw-Hill)