Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Simple and Inexpensive Perturbative Correction Schemes for Antisymmetric Products of Nonorthogonal Geminals – Supplementary Information

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1 Description and Scaling of the PT Algorithm

The central element in this kind of perturbation theory is the following system of linear equations

$$\sum_{K}^{\mathrm{D}} t_K \langle L|\hat{V} - E_0|K\rangle = -\langle L|\hat{H}|\psi\rangle + \frac{\langle L|\psi\rangle}{\langle 0|\psi\rangle}\langle 0|\hat{H}|\psi\rangle,$$

which has to be solved for the amplitudes t_K., Once all t_K are known, the second-order energy correction is obtained in a straightforward way as

$$E_2 = \sum_{K}^{\mathrm{D}} t_K \frac{\langle 0|\hat{H}|K\rangle}{\langle 0|\psi\rangle}$$

for PTa and

$$E_2 = \sum_{K}^{\mathrm{D}\backslash\mathrm{P}} t_K \langle \psi|\hat{H}|K\rangle$$

for PTb, respectively. The problem can be formulated as a matrix-vector product equation $\mathbf{At} = \mathbf{b}$ with $A_{LK} = \langle L|\hat{V} - E_0|K\rangle$ and $b_L = -\langle L|\hat{H}|\psi\rangle + \frac{\langle L|\psi\rangle}{\langle 0|\psi\rangle}\langle 0|\hat{H}|\psi\rangle$, which is solved iteratively using the Jacobi method, since $\mathbf{A}$ is diagonally dominant. The time critical step is the construction of the left-hand side $\mathbf{At}$, which is a weighted summation of Fock matrix elements. Since the summation is truncated to doubly-excited determinants, the number of elements in $\mathbf{t}$ is $O(n^4)$. $\mathbf{A}$ is a sparse matrix with only $O(n)$ nonzero elements per row (determinants that differ in maximally one orbital), such that the overall number of operations is $O(n^5)$. The largest memory allocations are needed for the storage of vectors $\mathbf{b}$ and $\mathbf{t}$, which makes the memory scaling with $O(n^4)$.

2 Generalized Matrix Element Expressions

In the following, the expressions for $\langle L|\hat{H}|\psi\rangle$ and $\langle L|\psi\rangle$ are given for a completely arbitrary closed-shell wavefunction $|\psi\rangle$ in terms of one- and two-particle matrix elements (h_{pq} and g_{pqrs}). The expressions are presented for most generalized matrix elements, which allows an implementation for unrestricted and even generalized complex orbitals. The only symmetry in the two-particle matrix that is assumed to hold is $g_{pqrs} = g_{qpsr}$. We use physicists' notation throughout.

2.1 Definitions

- Orbital indices i, j, k, l stand for occupied levels and a, b, c, d for virtual levels with respect to the reference determinant $\langle 0|$. Indices p, q, r, s are used for arbitrary orbitals.
- Even if the orbitals are completely generalized, it is practical to group them in pairs of 'quasi' α $(ijab)$ and 'quasi' β spin $(\bar{\imath}\bar{\jmath}\bar{a}\bar{b})$, due to the inherent paired nature of closed-shell wavefunctions.
- The determinants on which $|\psi\rangle$ is projected are denoted as excitations from the reference determinant $\langle 0|$ and abbreviated as $\langle {}^{a}_{i}| = \langle 0|a^{\dagger}_{i}a_{a}$, $\langle {}^{ab}_{ij}| = \langle 0|a^{\dagger}_{i}a^{\dagger}_{j}a_{b}a_{a}$, *etc.*
- The orbitals are sorted $\{1, \bar{1}, 2, \bar{2}, \ldots, i, \bar{\imath}, \ldots, j, \bar{\jmath}, \ldots, \ldots, a, \bar{a}, \ldots, b, \bar{b}, \ldots\}$, which makes all determinants unique. There is *e.g.* no determinant $\langle {}^{b\bar{a}}_{\bar{\imath}i}|$, as this is the same as $\langle {}^{\bar{a}b}_{i\bar{\imath}}|$.
- $\langle pq||rs\rangle = g_{pqrs} - g_{pqsr}$ denotes the antisymmetric two-electron integral.

2.2 Overlap

The overlap of arbitrary closed-shell determinants with $|\psi\rangle$ is

$$c_0 = \langle 0|\psi\rangle \qquad c^{a}_{i} = \langle {}^{a\bar{a}}_{i\bar{\imath}}|\psi\rangle \qquad c^{ab}_{ij} = \langle {}^{a\bar{a}b\bar{b}}_{i\bar{\imath}j\bar{\jmath}}|\psi\rangle$$

whereas all open-shell configuration coefficients are zero: $\langle {}^{a}_{i}|\psi\rangle = \langle {}^{\bar{a}}_{i}|\psi\rangle = \langle {}^{a}_{\bar{\imath}}|\psi\rangle = \langle {}^{\bar{a}}_{\bar{\imath}}|\psi\rangle = \langle {}^{a\bar{b}}_{i\bar{\imath}}|\psi\rangle = \langle {}^{a\bar{a}}_{ij}|\psi\rangle = \langle {}^{ab}_{ij}|\psi\rangle = \ldots = 0$.

In the case of AP1roG, the wavefunction has the additional features that intermediate normalization holds ($c_0 = 1$), and all quadruple and higher excitations are expressed by combinations of pair-excitations, *e.g.* $c^{ab}_{ij} = c^{a}_{i}c^{b}_{j} + c^{b}_{i}c^{a}_{j}$, such that all expansion coefficients of $|\psi\rangle$ are defined by the parameters $\{c^{a}_{i}\}$.

2.2.1 Seniority Zero

Projection onto seniority zero states yields all the JK-only matrix elements

$$\begin{aligned}
\langle 0|H|\psi\rangle &= \sum_{i}^{\text{occ.}}\left(h_{ii}+h_{\bar{\imath}\bar{\imath}}+\langle i\bar{\imath}||i\bar{\imath}\rangle+\sum_{j>i}^{\text{occ.}}\langle ij||ij\rangle+\langle\bar{\imath}\bar{\jmath}||\bar{\imath}\bar{\jmath}\rangle+\langle i\bar{\jmath}||i\bar{\jmath}\rangle+\langle\bar{\imath}j||\bar{\imath}j\rangle\right)c_0+\sum_{i}^{\text{occ.}}\sum_{a}^{\text{vir.}}\langle i\bar{\imath}||a\bar{a}\rangle c_i^a \\
\langle{}^{a\bar{a}}_{i\bar{\imath}}|H|\psi\rangle &= \sum_{j\neq i,j=a}^{\text{occ.}}\left(h_{jj}+h_{\bar{\jmath}\bar{\jmath}}+\langle j\bar{\jmath}||j\bar{\jmath}\rangle+\sum_{k>j,k\neq i,k=a}^{\text{occ.}}\langle jk||jk\rangle+\langle\bar{\jmath}\bar{k}||\bar{\jmath}\bar{k}\rangle+\langle j\bar{k}||j\bar{k}\rangle+\langle\bar{\jmath}k||\bar{\jmath}k\rangle\right)c_i^a \\
&\quad+\langle a\bar{a}||i\bar{\imath}\rangle c_0+\sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||i\bar{\imath}\rangle c_j^a+\sum_{b\neq a}^{\text{vir.}}\langle a\bar{a}||b\bar{b}\rangle c_i^b+\sum_{j\neq i}^{\text{occ.}}\sum_{b\neq a}^{\text{vir.}}\langle j\bar{\jmath}||b\bar{b}\rangle c_{ij}^{ab}.
\end{aligned}$$

With the aid of the Fock matrix elements, defined as $f_{pq}=h_{pq}+\sum_i^{\text{occ.}}\langle pi||qi\rangle+\langle p\bar{\imath}||q\bar{\imath}\rangle$, some computational time is saved and in addition the matrix elements can be written in an easier way as

$$\begin{aligned}
\langle 0|H|\psi\rangle &= \sum_{i}^{\text{occ.}}\left(h_{ii}+f_{ii}+h_{\bar{\imath}\bar{\imath}}+f_{\bar{\imath}\bar{\imath}}\right)\frac{c_0}{2}+\sum_{i}^{\text{occ.}}\sum_{a}^{\text{vir.}}\langle i\bar{\imath}||a\bar{a}\rangle c_i^a \\
\langle{}^{a\bar{a}}_{i\bar{\imath}}|H|\psi\rangle &= \sum_{j\neq i,j=a}^{\text{occ.}}\big(h_{jj}+f_{jj}+h_{\bar{\jmath}\bar{\jmath}}+f_{\bar{\jmath}\bar{\jmath}}-\langle ji||ji\rangle-\langle\bar{\jmath}\bar{\imath}||\bar{\jmath}\bar{\imath}\rangle-\langle j\bar{\imath}||j\bar{\imath}\rangle-\langle\bar{\jmath}i||\bar{\jmath}i\rangle+\langle ja||ja\rangle+\langle\bar{\jmath}\bar{a}||\bar{\jmath}\bar{a}\rangle \\
&\quad+\langle j\bar{a}||j\bar{a}\rangle+\langle\bar{\jmath}a||\bar{\jmath}a\rangle\big)\frac{c_i^a}{2}+\langle a\bar{a}||i\bar{\imath}\rangle c_0+\sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||i\bar{\imath}\rangle c_j^a+\sum_{b\neq a}^{\text{vir.}}\langle a\bar{a}||b\bar{b}\rangle c_i^b+\sum_{j\neq i}^{\text{occ.}}\sum_{b\neq a}^{\text{vir.}}\langle j\bar{\jmath}||b\bar{b}\rangle c_{ij}^{ab}.
\end{aligned}$$

2.2.2 Seniority Two

Up to double excitation, the seniority two determinants are $\langle{}^{a}_{i}|$, $\langle{}^{\bar{a}}_{i}|$, $\langle{}^{a}_{\bar{\imath}}|$, $\langle{}^{\bar{a}}_{\bar{\imath}}|$, $\langle{}^{ab}_{i\bar{\imath}}|$, $\langle{}^{a\bar{b}}_{i\bar{\imath}}|$, $\langle{}^{\bar{a}b}_{i\bar{\imath}}|$, $\langle{}^{\bar{a}\bar{b}}_{i\bar{\imath}}|$, $\langle{}^{a\bar{a}}_{ij}|$, $\langle{}^{a\bar{a}}_{i\bar{\jmath}}|$, $\langle{}^{a\bar{a}}_{\bar{\imath}j}|$ and $\langle{}^{a\bar{a}}_{\bar{\imath}\bar{\jmath}}|$. They can reach the following seniority zero states by single excitation:

$$\begin{aligned}
\langle{}^{a}_{i}|H|0\rangle &= h_{ai}+\langle a\bar{\imath}||i\bar{\imath}\rangle+\sum_{j\neq i}^{\text{occ.}}\langle aj||ij\rangle+\langle a\bar{\jmath}||i\bar{\jmath}\rangle=f_{ai} \\
\langle{}^{a}_{i}|H|{}^{a\bar{a}}_{i\bar{\imath}}\rangle=\langle{}^{a\bar{a}}_{i\bar{\imath}}|a_{\bar{a}}^{\dagger}a_{\bar{\imath}}H|{}^{a\bar{a}}_{i\bar{\imath}}\rangle &= h_{\bar{\imath}\bar{a}}+\langle\bar{\imath}a||\bar{a}a\rangle+\sum_{j\neq i}^{\text{occ.}}\langle\bar{\imath}j||\bar{a}j\rangle+\langle\bar{\imath}\bar{\jmath}||\bar{a}\bar{\jmath}\rangle=f_{\bar{\imath}\bar{a}}-\langle\bar{\imath}i||\bar{a}i\rangle+\langle\bar{\imath}a||\bar{a}a\rangle
\end{aligned}$$

$$\begin{aligned}
\langle{}^{a\bar{b}}_{i\bar{\imath}}|H|^{a\bar{a}}_{i\bar{\imath}}\rangle = \langle{}^{a\bar{a}}_{i\bar{\imath}}|a^\dagger_{\bar{a}}a_{\bar{b}}H|^{a\bar{a}}_{i\bar{\imath}}\rangle &= h_{\bar{b}\bar{a}} + \langle\bar{b}a||\bar{a}a\rangle + \sum_{j\neq i}^{\text{occ.}}\langle\bar{b}j||\bar{a}j\rangle + \langle\bar{b}\bar{\jmath}||\bar{a}\bar{\jmath}\rangle \\
&= f_{\bar{b}\bar{a}} - \langle\bar{b}i||\bar{a}i\rangle - \langle\bar{b}\bar{\imath}||\bar{a}\bar{\imath}\rangle + \langle\bar{b}a||\bar{a}a\rangle \\
\langle{}^{a\bar{b}}_{i\bar{\imath}}|H|^{b\bar{b}}_{i\bar{\imath}}\rangle = \langle{}^{b\bar{b}}_{i\bar{\imath}}|a^\dagger_{b}a_{a}H|^{b\bar{b}}_{i\bar{\imath}}\rangle &= h_{ab} + \langle a\bar{b}||b\bar{b}\rangle + \sum_{j\neq i}^{\text{occ.}}\langle aj||bj\rangle + \langle a\bar{\jmath}||b\bar{\jmath}\rangle \\
&= f_{ab} - \langle ai||bi\rangle - \langle a\bar{\imath}||b\bar{\imath}\rangle + \langle a\bar{b}||b\bar{b}\rangle \\
\langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|^{a\bar{a}}_{i\bar{\imath}}\rangle = -\langle{}^{a\bar{a}}_{i\bar{\imath}}|a^\dagger_{\bar{\jmath}}a_{\bar{\imath}}H|^{a\bar{a}}_{i\bar{\imath}}\rangle &= -\left(h_{\bar{\imath}\bar{\jmath}} + \langle\bar{\imath}j||\bar{\jmath}j\rangle + \sum_{k\neq i,j;k=a}^{\text{occ.}}\langle\bar{\imath}k||\bar{\jmath}k\rangle + \langle\bar{\imath}\bar{k}||\bar{\jmath}\bar{k}\rangle\right) \\
&= -f_{\bar{\imath}\bar{\jmath}} - \langle\bar{\imath}a||\bar{\jmath}a\rangle - \langle\bar{\imath}\bar{a}||\bar{\jmath}\bar{a}\rangle + \langle\bar{\imath}i||\bar{\jmath}i\rangle \\
\langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|^{a\bar{a}}_{j\bar{\jmath}}\rangle = -\langle{}^{a\bar{a}}_{j\bar{\jmath}}|a^\dagger_{i}a_{j}H|^{a\bar{a}}_{j\bar{\jmath}}\rangle &= -\left(h_{ji} + \langle j\bar{\imath}||i\bar{\imath}\rangle + \sum_{k\neq i,j;k=a}^{\text{occ.}}\langle jk||ik\rangle + \langle j\bar{k}||i\bar{k}\rangle\right) \\
&= -f_{ji} - \langle ja||ia\rangle - \langle j\bar{a}||i\bar{a}\rangle + \langle j\bar{\jmath}||i\bar{\jmath}\rangle.
\end{aligned}$$

Together with the double excitations

$$\begin{aligned}
&\langle{}^{a}_{i}|H|^{b\bar{b}}_{i\bar{\imath}}\rangle = \langle a\bar{\imath}||b\bar{b}\rangle \qquad \langle{}^{a\bar{b}}_{i\bar{\imath}}|H|0\rangle = \langle a\bar{b}||i\bar{\imath}\rangle \qquad \langle{}^{a\bar{b}}_{i\bar{\imath}}|H|^{c\bar{c}}_{i\bar{\imath}}\rangle = \langle a\bar{b}||c\bar{c}\rangle \qquad \langle{}^{a\bar{b}}_{i\bar{\imath}}|H|^{a\bar{a}b\bar{b}}_{i\bar{\imath}j\bar{\jmath}}\rangle = -\langle j\bar{\jmath}||b\bar{a}\rangle \\
&\langle{}^{a}_{i}|H|^{a\bar{a}}_{j\bar{\jmath}}\rangle = -\langle j\bar{\jmath}||i\bar{a}\rangle \qquad \langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|0\rangle = \langle a\bar{a}||i\bar{\jmath}\rangle \qquad \langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|^{a\bar{a}}_{k\bar{k}}\rangle = \langle k\bar{k}||i\bar{\jmath}\rangle \qquad \langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|^{a\bar{a}b\bar{b}}_{i\bar{\imath}j\bar{\jmath}}\rangle = -\langle\bar{\imath}j||\bar{b}b\rangle
\end{aligned}$$

we can construct the seniority two matrix elements as

$$\begin{aligned}
\langle{}^{a}_{i}|H|\psi\rangle &= \left(h_{ai} + \langle a\bar{\imath}||i\bar{\imath}\rangle + \sum_{j\neq i}^{\text{occ.}}\langle aj||ij\rangle + \langle a\bar{\jmath}||i\bar{\jmath}\rangle\right)c_0 + \left(h_{\bar{\imath}\bar{a}} + \langle\bar{\imath}a||\bar{a}a\rangle + \sum_{j\neq i}^{\text{occ.}}\langle\bar{\imath}j||\bar{a}j\rangle + \langle\bar{\imath}\bar{\jmath}||\bar{a}\bar{\jmath}\rangle\right)c_i^a \\
&\quad - \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||i\bar{a}\rangle c_j^a + \sum_{b\neq a}^{\text{vir.}}\langle a\bar{\imath}||b\bar{b}\rangle c_i^b \\
\langle{}^{a\bar{b}}_{i\bar{\imath}}|H|\psi\rangle &= \left(h_{\bar{b}\bar{a}} + \langle\bar{b}a||\bar{a}a\rangle + \sum_{j\neq i}^{\text{occ.}}\langle\bar{b}j||\bar{a}j\rangle + \langle\bar{b}\bar{\jmath}||\bar{a}\bar{\jmath}\rangle\right)c_i^a + \langle a\bar{b}||i\bar{\imath}\rangle c_0 + \sum_{c\neq a,b}^{\text{vir.}}\langle a\bar{b}||c\bar{c}\rangle c_i^c \\
&\quad + \left(h_{ab} + \langle a\bar{b}||b\bar{b}\rangle + \sum_{j\neq i}^{\text{occ.}}\langle aj||bj\rangle + \langle a\bar{\jmath}||b\bar{\jmath}\rangle\right)c_i^b - \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||b\bar{a}\rangle c_{ij}^{ab} \\
\langle{}^{a\bar{a}}_{i\bar{\jmath}}|H|\psi\rangle &= -\left(h_{\bar{\imath}\bar{\jmath}} + \langle\bar{\imath}j||\bar{\jmath}j\rangle + \sum_{k\neq i,j;k=a}^{\text{occ.}}\langle\bar{\imath}k||\bar{\jmath}k\rangle + \langle\bar{\imath}\bar{k}||\bar{\jmath}\bar{k}\rangle\right)c_i^a + \langle a\bar{a}||i\bar{\jmath}\rangle c_0 + \sum_{k\neq i,j}^{\text{occ.}}\langle k\bar{k}||i\bar{\jmath}\rangle c_k^a \\
&\quad - \left(h_{ji} + \langle j\bar{\imath}||i\bar{\imath}\rangle + \sum_{k\neq i,j;k=a}^{\text{occ.}}\langle jk||ik\rangle + \langle j\bar{k}||i\bar{k}\rangle\right)c_j^a - \sum_{b\neq a}^{\text{vir.}}\langle\bar{\imath}j||\bar{b}b\rangle c_{ij}^{ab}
\end{aligned}$$

or, applying the Fock matrix,

$$\begin{aligned}
\langle {}^{a}_{i}|H|\psi\rangle &= f_{ai}c_0 + \left(f_{\bar{\imath}\bar{a}} - \langle\bar{\imath}i||\bar{a}i\rangle + \langle\bar{\imath}a||\bar{a}a\rangle\right)c_i^a - \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||i\bar{a}\rangle c_j^a + \sum_{b\neq a}^{\text{vir.}}\langle a\bar{\imath}||b\bar{b}\rangle c_i^b \\
\langle {}^{a\bar{b}}_{i\bar{\imath}}|H|\psi\rangle &= \left(f_{\bar{b}\bar{a}} - \langle\bar{b}i||\bar{a}i\rangle - \langle\bar{b}\bar{\imath}||\bar{a}\bar{\imath}\rangle + \langle\bar{b}a||\bar{a}a\rangle\right)c_i^a + \left(f_{ab} - \langle ai||bi\rangle - \langle a\bar{\imath}||b\bar{\imath}\rangle + \langle a\bar{b}||b\bar{b}\rangle\right)c_i^b \\
&\quad + \langle a\bar{b}||i\bar{\imath}\rangle c_0 + \sum_{c\neq a,b}^{\text{vir.}}\langle a\bar{b}||c\bar{c}\rangle c_i^c - \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||b\bar{a}\rangle c_{ij}^{ab} \\
\langle {}^{a\bar{a}}_{i\bar{\jmath}}|H|\psi\rangle &= -\left(f_{\bar{\imath}\bar{\jmath}} + \langle\bar{\imath}a||\bar{\jmath}a\rangle + \langle\bar{\imath}\bar{a}||\bar{\jmath}\bar{a}\rangle - \langle\bar{\imath}i||\bar{\jmath}i\rangle\right)c_i^a - \left(f_{ji} + \langle ja||ia\rangle + \langle j\bar{a}||i\bar{a}\rangle - \langle j\bar{\jmath}||i\bar{\jmath}\rangle\right)c_j^a \\
&\quad + \langle a\bar{a}||i\bar{\jmath}\rangle c_0 + \sum_{k\neq i,j}^{\text{occ.}}\langle k\bar{k}||i\bar{\jmath}\rangle c_k^a - \sum_{b\neq a}^{\text{vir.}}\langle\bar{\imath}j||\bar{b}b\rangle c_{ij}^{ab}.
\end{aligned}$$

2.2.3 Seniority Four

For the seniority four states $\langle {}^{ab}_{ij}|$, and the other 15 spin-flipped states like $\langle {}^{\bar{a}b}_{ij}|$, $\langle {}^{a\bar{b}}_{i\bar{\jmath}}|$, $\langle {}^{\bar{a}b}_{i\bar{\jmath}}|$, $\langle {}^{\bar{a}\bar{b}}_{ij}|$, $\langle {}^{\bar{a}\bar{b}}_{\bar{\imath}\bar{\jmath}}|$, $\langle {}^{\bar{a}\bar{b}}_{\bar{\imath}\bar{\jmath}}|$, *etc.* only two-electron elements matter and we end up with

$$\langle {}^{ab}_{ij}|H|\psi\rangle = \langle ab||ij\rangle c_0 + \langle\bar{\imath}\bar{\jmath}||\bar{a}\bar{b}\rangle c_{ij}^{ab} + \langle\bar{\imath}b||\bar{a}j\rangle c_i^a + \langle\bar{\jmath}a||\bar{b}i\rangle c_j^b - \langle\bar{\imath}a||\bar{b}j\rangle c_i^b - \langle\bar{\jmath}b||\bar{a}i\rangle c_j^a.$$

2.3 Exchanging Paired Orbitals

For seniority two and four, the other determinants can be derived from above expressions by adhering to the following rules: If any of the orbitals i, j, a, b are replaced by its pairs $\bar{\imath}, \bar{\jmath}, \bar{a}, \bar{b}$, the indices in $\langle ij||ab\rangle$ have to be adapted, and the sign of the corresponding coefficient c changes, if the index is appearing in there. We have thus

$$
\begin{aligned}
\langle^{\bar{a}}_{\bar{\imath}}|H|\psi\rangle &= f_{\bar{a}\bar{\imath}}c_0 + (f_{ia} - \langle i\bar{\imath}||a\bar{\imath}\rangle + \langle i\bar{a}||a\bar{a}\rangle)\, c_i^a - \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||a\bar{\imath}\rangle c_j^a + \sum_{b\neq a}^{\text{vir.}}\langle i\bar{a}||b\bar{b}\rangle c_i^b \\
\langle^{\bar{a}}_{i}|H|\psi\rangle &= f_{\bar{a}i}c_0 - (f_{\bar{\imath}a} - \langle\bar{\imath}i||ai\rangle + \langle\bar{\imath}\bar{a}||a\bar{a}\rangle)\, c_i^a + \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||ia\rangle c_j^a + \sum_{b\neq a}^{\text{vir.}}\langle\bar{a}\bar{\imath}||b\bar{b}\rangle c_i^b \\
\langle^{a}_{\bar{\imath}}|H|\psi\rangle &= f_{a\bar{\imath}}c_0 - (f_{i\bar{a}} - \langle i\bar{\imath}||\bar{a}\bar{\imath}\rangle + \langle ia||\bar{a}a\rangle)\, c_i^a + \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||\bar{a}\bar{\imath}\rangle c_j^a + \sum_{b\neq a}^{\text{vir.}}\langle ia||b\bar{b}\rangle c_i^b \\
\langle^{\bar{a}b}_{i\bar{\imath}}|H|\psi\rangle &= -(f_{ba} - \langle bi||ai\rangle - \langle b\bar{\imath}||a\bar{\imath}\rangle + \langle b\bar{a}||a\bar{a}\rangle)\, c_i^a - \left(f_{\bar{a}\bar{b}} - \langle\bar{a}i||\bar{b}i\rangle - \langle\bar{a}\bar{\imath}||\bar{b}\bar{\imath}\rangle + \langle\bar{a}b||\bar{b}b\rangle\right) c_i^b \\
&\quad -\langle b\bar{a}||i\bar{\imath}\rangle c_0 - \sum_{c\neq a,b}^{\text{vir.}}\langle b\bar{a}||c\bar{c}\rangle c_i^c + \sum_{j\neq i}^{\text{occ.}}\langle j\bar{\jmath}||a\bar{b}\rangle c_{ij}^{ab} \\
&\ \ \vdots
\end{aligned}
$$

for seniority two states and

$$
\begin{aligned}
\langle^{\bar{a}b}_{ij}|H|\psi\rangle &= \langle\bar{a}b||ij\rangle c_0 - \langle\bar{\imath}\bar{\jmath}||a\bar{b}\rangle c_{ij}^{ab} - \langle\bar{\imath}b||aj\rangle c_i^a + \langle\bar{\jmath}a||\bar{b}i\rangle c_j^b - \langle\bar{\imath}a||\bar{b}j\rangle c_i^b + \langle\bar{\jmath}b||ai\rangle c_j^a \\
\langle^{a\bar{b}}_{i\bar{\jmath}}|H|\psi\rangle &= \langle a\bar{b}||i\bar{\jmath}\rangle c_0 + \langle\bar{\imath}j||\bar{a}b\rangle c_{ij}^{ab} + \langle\bar{\imath}\bar{b}||\bar{a}\bar{\jmath}\rangle c_i^a + \langle ja||bi\rangle c_j^b + \langle\bar{\imath}a||b\bar{\jmath}\rangle c_i^b + \langle j\bar{b}||\bar{a}i\rangle c_j^a \\
\langle^{\bar{a}b}_{i\bar{\jmath}}|H|\psi\rangle &= \langle\bar{a}b||i\bar{\jmath}\rangle c_0 + \langle\bar{\imath}j||a\bar{b}\rangle c_{ij}^{ab} - \langle\bar{\imath}b||a\bar{\jmath}\rangle c_i^a - \langle j\bar{a}||\bar{b}i\rangle c_j^b - \langle\bar{\imath}a||\bar{b}\bar{\jmath}\rangle c_i^b - \langle jb||ai\rangle c_j^a \\
\langle^{\bar{a}\bar{b}}_{ij}|H|\psi\rangle &= \langle\bar{a}\bar{b}||\bar{\imath}j\rangle c_0 + \langle\bar{\imath}\bar{\jmath}||ab\rangle c_{ij}^{ab} - \langle\bar{\imath}\bar{b}||aj\rangle c_i^a - \langle\bar{\jmath}a||bi\rangle c_j^b + \langle\bar{\imath}a||bj\rangle c_i^b + \langle\bar{\jmath}\bar{b}||ai\rangle c_j^a \\
\langle^{\bar{a}\bar{b}}_{\bar{\imath}j}|H|\psi\rangle &= \langle\bar{a}\bar{b}||\bar{\imath}j\rangle c_0 - \langle i\bar{\jmath}||ab\rangle c_{ij}^{ab} + \langle i\bar{b}||aj\rangle c_i^a - \langle\bar{\jmath}a||b\bar{\imath}\rangle c_j^b - \langle i\bar{a}||bj\rangle c_i^b + \langle\bar{\jmath}\bar{b}||a\bar{\imath}\rangle c_j^a \\
\langle^{\bar{a}\bar{b}}_{\bar{\imath}\bar{\jmath}}|H|\psi\rangle &= \langle\bar{a}\bar{b}||\bar{\imath}\bar{\jmath}\rangle c_0 + \langle ij||ab\rangle c_{ij}^{ab} + \langle i\bar{b}||a\bar{\jmath}\rangle c_i^a + \langle j\bar{a}||b\bar{\imath}\rangle c_j^b - \langle i\bar{a}||b\bar{\jmath}\rangle c_i^b - \langle j\bar{b}||a\bar{\imath}\rangle c_j^a \\
&\ \ \vdots
\end{aligned}
$$

for seniority four states. These expressions can describe the entire set of determinants that directly couple to the reference state $|0\rangle$.

2.4 Simplifications

2.4.1 Spin Restriction

Using restricted orbitals, the additional equalities $h_{pq} = h_{\bar{p}\bar{q}}$, $g_{pqrs} = g_{p\bar{q}r\bar{s}} = g_{\bar{p}qr\bar{s}} = g_{\bar{p}\bar{q}\bar{r}\bar{s}}$ and $h_{p\bar{q}} = g_{pqr\bar{s}} = g_{p\bar{q}\bar{r}s} = \ldots = 0$ hold. This simplifies the seniority zero states to

$$\begin{aligned}
\langle 0|H|\psi\rangle &= \sum_{i}^{\text{occ.}} (h_{ii} + f_{ii})\, c_0 + \sum_{i}^{\text{occ.}} \sum_{a}^{\text{vir.}} g_{iiaa} c_i^a \\
\langle {}^{a\bar{a}}_{i\bar{i}}|H|\psi\rangle &= \sum_{j\neq i, j=a}^{\text{occ.}} (h_{jj} + f_{jj} - 2g_{jiji} + g_{jiij} + 2g_{jaja} - g_{jaaj})\, c_i^a \\
&\quad + g_{aaii} c_0 + \sum_{j\neq i}^{\text{occ.}} g_{jjii} c_j^a + \sum_{b\neq a}^{\text{vir.}} g_{aabb} c_i^b + \sum_{j\neq i}^{\text{occ.}} \sum_{b\neq a}^{\text{vir.}} g_{jjbb} c_{ij}^{ab}.
\end{aligned}$$

For seniority two, the only surviving states in the projection space are the singlet linear combinations $\langle {}^a_i| + \langle {}^{\bar{a}}_{\bar{i}}|$, $\langle {}^{a\bar{b}}_{i\bar{i}}| + \langle {}^{\bar{a}b}_{\bar{i}i}|$, and $\langle {}^{a\bar{a}}_{i\bar{j}}| + \langle {}^{\bar{a}a}_{\bar{i}j}|$, whose normalized expressions become

$$\begin{aligned}
\frac{\langle {}^a_i| + \langle {}^{\bar{a}}_{\bar{i}}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\Bigg[f_{ai} c_0 + (f_{ia} - g_{iiia} + g_{iaaa})\, c_i^a - \sum_{j\neq i}^{\text{occ.}} g_{jjia} c_j^a + \sum_{b\neq a}^{\text{vir.}} g_{iabb} c_i^b \Bigg] \\
\frac{\langle {}^{a\bar{b}}_{i\bar{i}}| + \langle {}^{\bar{a}b}_{\bar{i}i}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\Bigg[(f_{ba} - 2g_{biai} + g_{biia} + g_{baaa})\, c_i^a + (f_{ab} - 2g_{aibi} + g_{aiib} + g_{abbb})\, c_i^b \\
&\quad + g_{abii} c_0 + \sum_{c\neq a,b}^{\text{vir.}} g_{abcc} c_i^c - \sum_{j\neq i}^{\text{occ.}} g_{jjab} c_{ij}^{ab} \Bigg] \\
\frac{\langle {}^{a\bar{a}}_{i\bar{j}}| + \langle {}^{\bar{a}a}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\Bigg[- (f_{ij} + 2g_{iaja} - g_{iaaj} - g_{iiij})\, c_i^a - (f_{ji} + 2g_{jaia} - g_{jaai} - g_{jjji})\, c_j^a \\
&\quad + g_{aaij} c_0 + \sum_{k\neq i,j}^{\text{occ.}} g_{kkij} c_k^a - \sum_{b\neq a}^{\text{vir.}} g_{ijbb} c_{ij}^{ab} \Bigg].
\end{aligned}$$

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It remains the treatment of the seniority four states with the singlet states

$$
\begin{aligned}
\frac{\langle^{ab}_{ij}| + \langle^{\bar{a}\bar{b}}_{\bar{i}\bar{j}}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\left[(g_{abij} - g_{abji})c_0 + (g_{ijab} - g_{ijba})c^{ab}_{ij} + g_{ibaj}c^a_i + g_{jabi}c^b_j - g_{iabj}c^b_i - g_{jbai}c^a_j\right] \\
\frac{\langle^{a\bar{b}}_{i\bar{j}}| + \langle^{\bar{a}b}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\left[g_{abij}c_0 + g_{ijab}c^{ab}_{ij} + (g_{ibaj} - g_{ibja})c^a_i + (g_{jabi} - g_{jaib})c^b_j - g_{iajb}c^b_i - g_{jbia}c^a_j\right] \\
\frac{\langle^{\bar{a}b}_{i\bar{j}}| + \langle^{a\bar{b}}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\left[-g_{abji}c_0 - g_{ijba}c^{ab}_{ij} + g_{ibja}c^a_i + g_{jaib}c^b_j + (g_{iajb} - g_{iabj})c^b_i + (g_{jbia} - g_{jbai})c^a_j\right].
\end{aligned}
$$

2.4.2 Real Matrix Elements

Finally forcing the matrix element to be real and symmetric, we introduce another set of equalities $h_{pq} = h_{qp}$ and $g_{pqrs} = g_{rspq} = g_{psrq} = g_{rqps}$ which simplifies seniority two and four (but not seniority zero) to

$$
\begin{aligned}
\frac{\langle^{a}_{i}| + \langle^{\bar{a}}_{\bar{i}}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\left[f_{ia}\left(c_0 + c^a_i\right) + \left(g_{iaaa} - g_{iiia}\right)c^a_i - \sum_{j\neq i}^{\text{occ.}} g_{iajj}c^a_j + \sum_{b\neq a}^{\text{vir.}} g_{iabb}c^b_i\right] \\
\frac{\langle^{a\bar{b}}_{i\bar{i}}| + \langle^{\bar{a}b}_{\bar{i}i}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\Bigg[\left(f_{ab} - 2g_{iaib} + g_{iabi}\right)\left(c^a_i + c^b_i\right) + g_{aaab}c^a_i + g_{abbb}c^b_i \\
&\quad + g_{abii}c_0 + \sum_{c\neq a,b}^{\text{vir.}} g_{abcc}c^c_i - \sum_{j\neq i}^{\text{occ.}} g_{jjab}c^{ab}_{ij}\Bigg] \\
\frac{\langle^{a\bar{a}}_{i\bar{j}}| + \langle^{\bar{a}a}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}\Bigg[-\left(f_{ij} + 2g_{iaja} - g_{iaaj}\right)\left(c^a_i + c^a_j\right) + g_{iiij}c^a_i + g_{ijjj}c^a_j \\
&\quad + g_{ijaa}c_0 + \sum_{k\neq i,j}^{\text{occ.}} g_{ijkk}c^a_k - \sum_{b\neq a}^{\text{vir.}} g_{ijbb}c^{ab}_{ij}\Bigg] \\
\frac{\langle^{ab}_{ij}| + \langle^{\bar{a}\bar{b}}_{\bar{i}\bar{j}}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}g_{ijab}\left(c_0 + c^{ab}_{ij} + c^a_i + c^b_j\right) - \sqrt{2}g_{ijba}\left(c_0 + c^{ab}_{ij} + c^b_i + c^a_j\right) \\
\frac{\langle^{a\bar{b}}_{i\bar{j}}| + \langle^{\bar{a}b}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}g_{ijab}\left(c_0 + c^{ab}_{ij} + c^a_i + c^b_j\right) - \sqrt{2}g_{iajb}\left(c^a_i + c^b_j + c^b_i + c^a_j\right) \\
\frac{\langle^{\bar{a}b}_{i\bar{j}}| + \langle^{a\bar{b}}_{\bar{i}j}|}{\sqrt{2}} H|\psi\rangle &= \sqrt{2}g_{iajb}\left(c^a_i + c^b_j + c^b_i + c^a_j\right) - \sqrt{2}g_{ijba}\left(c_0 + c^{ab}_{ij} + c^b_i + c^a_j\right).
\end{aligned}
$$

These are the equations that were used to generate the numerical results presented in the article.