

Exam in Advanced Quantum Chemistry – Part 2 (18 points)

January 2020

2. Seniority-zero many-body wavefunctions (10 points)

An N -electron many-body wavefunction $\tilde{\Psi}$ is said to have no seniority (hence its name “seniority-zero wavefunction”) if it can be written as a linear combination of Slater determinants \mathcal{D} in which *orbitals are either doubly occupied or not occupied at all*:

$$|\tilde{\Psi}\rangle = \sum_{\mathcal{D}} C_{\mathcal{D}} |\mathcal{D}\rangle, \quad (1)$$

where

$$|\mathcal{D}\rangle = \left| (p_1)^2 (p_2)^2 \dots \left(p_{\frac{N}{2}} \right)^2 \right\rangle \equiv \prod_{i=1}^{\frac{N}{2}} \hat{a}_{p_i, \alpha}^\dagger \hat{a}_{p_i, \beta}^\dagger |\text{vac}\rangle. \quad (2)$$

- a) [1 pt] Can we use the ansatz of Eqs. (1) and (2) for describing electron correlation? Justify your answer by referring, for example, to the MP2 wavefunction.

Yes. In the MP2 method, for example, the correlated wavefunction consists of the reference HF determinant (which is a seniority-zero wavefunction in the closed-shell case) to which a linear combination of doubly-excited determinants is added. Among all the possible double excitations, the following will preserve the seniority-zero character of the wavefunction: $i^2 \rightarrow a^2$, where i and a denote occupied and virtual orbitals in the HF determinant, respectively. Note that some double excitations like, for example, $(i\alpha, j\beta) \rightarrow a^2$, where $i \neq j$, are not taken into account in a seniority-zero wavefunction.

- b) [1 pt] Show, by considering the simple example of the stretched H_2 molecule, that seniority-zero wavefunctions are well adapted to the description of strong correlation effects.

In the dissociation limit of H_2 , the ground state is strongly correlated (one electron is localized on one hydrogen atom while the other electron is localized on the other atom). Since the exact ground-state wavefunction reads $|\Psi_0\rangle = \frac{1}{\sqrt{2}} (|\sigma_g^2\rangle - |\sigma_u^2\rangle)$, where σ_g and σ_u are the bonding and antibonding orbitals, respectively, we conclude that, in this simple example, the strongly correlated ground state has no seniority.

- c) [1.5 pts] In the following, we consider a single set of molecular orbitals $\{\varphi_p\}_p$ from which all the seniority-zero Slater determinants \mathcal{D} are constructed. Let us first assume that these orbitals are Hartree–Fock

orbitals. A configuration interaction (CI) calculation based on the wavefunction ansatz of Eq. (1) is referred to as *doubly occupied* CI (DOCI). Explain briefly how the coefficients $C_{\mathcal{D}}$ and the ground-state energy would be determined within the DOCI method.

DOCI is a CI calculation where the energy (and the seniority-zero CI coefficients $C_{\mathcal{D}}$) will be obtained by diagonalizing the projection of the Hamiltonian matrix onto the space of seniority-zero determinants. The latter can be obtained by applying all possible seniority-zero-preserving excitations to the reference HF determinant (doubles, quadruples, sextuples, etc ...).

Is DOCI equivalent to full CI (FCI)?

No because many excitations like singles or triples will be absent from a DOCI calculation. Indeed these excitations do not preserve the seniority.

- d) [1 pt] In the spirit of the *multiconfigurational self-consistent field* (MCSCF) method, one may opt for a reoptimization of the orbitals within a DOCI calculation. Explain how this could be achieved by means of an orbital rotation operator.

In such a seniority-zero MCSCF approach, the wavefunction would be parameterized as follows:

$$|\tilde{\Psi}(\boldsymbol{\kappa}, \mathbf{C})\rangle = e^{-\hat{\kappa}} \left(\sum_{\mathcal{D}} C_{\mathcal{D}} |\mathcal{D}\rangle \right), \quad (3)$$

where $\hat{\kappa} = \sum_{p>q,\sigma} \kappa_{pq} (\hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} - \hat{a}_{q,\sigma}^\dagger \hat{a}_{p,\sigma})$, and the variational parameters are $\boldsymbol{\kappa} \equiv \{\kappa_{pq}\}_{p>q}$ and $\mathbf{C} \equiv \{C_{\mathcal{D}}\}_{\mathcal{D}}$. Their optimal values would be obtained by minimizing the following seniority-zero energy:

$$\mathcal{E}(\boldsymbol{\kappa}, \mathbf{C}) = \frac{\langle \tilde{\Psi}(\boldsymbol{\kappa}, \mathbf{C}) | \hat{H} | \tilde{\Psi}(\boldsymbol{\kappa}, \mathbf{C}) \rangle}{\langle \tilde{\Psi}(\boldsymbol{\kappa}, \mathbf{C}) | \tilde{\Psi}(\boldsymbol{\kappa}, \mathbf{C}) \rangle}. \quad (4)$$

- e) [2 pts] Let us consider the (so-called *one-electron reduced*) density matrix elements:

$$D_{pq}^{\tilde{\Psi}} = \sum_{\sigma=\alpha,\beta} \langle \tilde{\Psi} | \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \tilde{\Psi} \rangle. \quad (5)$$

Prove that, according to Eq. (1), the density matrix is diagonal

$$D_{pq}^{\tilde{\Psi}} = \sum_{\mathcal{D}, \mathcal{D}'} C_{\mathcal{D}} C_{\mathcal{D}'} \sum_{\sigma=\alpha,\beta} \langle \mathcal{D}' | \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \mathcal{D} \rangle. \quad (6)$$

If $p \neq q$, various scenarios should be considered. If q is not occupied in \mathcal{D} or p is (doubly) occupied in \mathcal{D} then $\hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \mathcal{D} \rangle = -\hat{a}_{q,\sigma} \hat{a}_{p,\sigma}^\dagger | \mathcal{D} \rangle = 0$. If q is occupied and p is unoccupied then $\hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \mathcal{D} \rangle$ is not

zero but it is not a seniority-zero determinant (since p and q are now singly occupied). It is therefore orthogonal to all seniority-zero determinants \mathcal{D}' . In conclusion, in all cases, $\langle \mathcal{D}' | \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \mathcal{D} \rangle = 0$ when $p \neq q$.

and the diagonal elements read

$$n_p^{\tilde{\Psi}} = D_{pp}^{\tilde{\Psi}} = 2 \sum_{\mathcal{D} \ni p} C_{\mathcal{D}}^2, \quad (7)$$

where “ $\mathcal{D} \ni p$ ” means that the sum runs over the seniority-zero Slater determinants \mathcal{D} in which the orbital φ_p is (doubly) occupied.

$$D_{pp}^{\tilde{\Psi}} = \sum_{\mathcal{D}, \mathcal{D}'} C_{\mathcal{D}} C_{\mathcal{D}'} \langle \mathcal{D}' | \hat{n}_p | \mathcal{D} \rangle, \quad (8)$$

where $\hat{n}_p = \sum_{\sigma=\alpha,\beta} \hat{a}_{p,\sigma}^\dagger \hat{a}_{p,\sigma}$ is the occupation operator for orbital p . Since $\hat{n}_p | \mathcal{D} \rangle = n_p^{\mathcal{D}} | \mathcal{D} \rangle$ where $n_p^{\mathcal{D}} = 0$ if p is not occupied in \mathcal{D} and $n_p^{\mathcal{D}} = 2$ if it is (doubly) occupied, it comes

$$D_{pp}^{\tilde{\Psi}} = \sum_{\mathcal{D}, \mathcal{D}'} C_{\mathcal{D}} C_{\mathcal{D}'} n_p^{\mathcal{D}} \langle \mathcal{D}' | \mathcal{D} \rangle = \sum_{\mathcal{D}, \mathcal{D}'} C_{\mathcal{D}} C_{\mathcal{D}'} n_p^{\mathcal{D}} \delta_{\mathcal{D}' \mathcal{D}} = \sum_{\mathcal{D}} C_{\mathcal{D}}^2 n_p^{\mathcal{D}} = 2 \sum_{\mathcal{D} \ni p} C_{\mathcal{D}}^2. \quad (9)$$

What is the physical meaning of $n_p^{\tilde{\Psi}}$?

$n_p^{\tilde{\Psi}}$ is the occupation number of the orbital p in the seniority-zero wavefunction. Note that it is in principle fractional (it would be an integer if we were using a single Slater determinant instead of a linear combination of Slater determinants).

- f) [1 pt] Let us write the electronic Hamiltonian as $\hat{H} = \sum_{pq,\sigma=\alpha,\beta} h_{pq} \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} + \hat{W}_{ee}$ where \hat{W}_{ee} is the two-electron repulsion operator. What are the energy contributions described by the one-electron integrals h_{pq} ?

The kinetic energy and the nuclear attraction potential energy.

Show that $\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \sum_p v_p n_p^{\tilde{\Psi}} + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle$, where $v_p = h_{pp}$.

$$\begin{aligned}
\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle &= \sum_{pq, \sigma=\alpha, \beta} h_{pq} \langle \tilde{\Psi} | \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} | \tilde{\Psi} \rangle + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle, \\
&= \sum_{pq} h_{pq} D_{pq}^{\tilde{\Psi}} + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle \\
&= \sum_{pq} h_{pq} n_p^{\tilde{\Psi}} \delta_{pq} + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle \\
&= \sum_p h_{pp} n_p^{\tilde{\Psi}} + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle.
\end{aligned} \tag{10}$$

g) [2.5 pts] Let \mathcal{E}_0 be the seniority-zero ground-state energy:

$$\mathcal{E}_0 = \min_{\tilde{\Psi}} \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle = \sum_p v_p n_p^{\tilde{\Psi}_0} + \langle \tilde{\Psi}_0 | \hat{W}_{ee} | \tilde{\Psi}_0 \rangle, \tag{11}$$

where the minimization is restricted to *normalized* seniority-zero wavefunctions $\tilde{\Psi}$ [we assume that the orbitals are fixed]. By changing the diagonal elements of the one-electron integrals, i.e. $v_p \rightarrow h'_{pp} = v'_p$, we obtain a new ground-state seniority-zero wavefunction $\tilde{\Psi}'_0$, new occupations $n_p^{\tilde{\Psi}'_0}$, and therefore a new seniority-zero ground-state energy \mathcal{E}'_0 . We assume that ground states are *not degenerate* and that they have exactly the same orbital occupations, i.e. $n_p^{\tilde{\Psi}'_0} = n_p^{\tilde{\Psi}_0} = n_p^0$. Prove that, under these assumptions, $\mathcal{E}_0 < \mathcal{E}'_0 + \sum_p (v_p - v'_p) n_p^0$ and $\mathcal{E}'_0 < \mathcal{E}_0 - \sum_p (v_p - v'_p) n_p^0$.

If we assume that seniority-zero ground-state wavefunctions are not degenerate, applying the variational principle of Eq. (11) to both Hamiltonians with v_p and v'_p diagonal one-electron integral elements leads to

$$\mathcal{E}_0 < \langle \tilde{\Psi}'_0 | \sum_{pq, \sigma=\alpha, \beta} h_{pq} \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} + \hat{W}_{ee} | \tilde{\Psi}'_0 \rangle \tag{12}$$

and

$$\mathcal{E}'_0 < \langle \tilde{\Psi}_0 | \sum_{pq, \sigma=\alpha, \beta} h'_{pq} \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} + \hat{W}_{ee} | \tilde{\Psi}_0 \rangle, \tag{13}$$

where

$$\begin{aligned}
\langle \tilde{\Psi}'_0 | \sum_{pq, \sigma=\alpha, \beta} h_{pq} \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} + \hat{W}_{ee} | \tilde{\Psi}'_0 \rangle &= \langle \tilde{\Psi}'_0 | \sum_{pq, \sigma=\alpha, \beta} h'_{pq} \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} + \hat{W}_{ee} | \tilde{\Psi}'_0 \rangle \\
&\quad + \langle \tilde{\Psi}'_0 | \sum_{pq, \sigma=\alpha, \beta} (h_{pq} - h'_{pq}) \hat{a}_{p, \sigma}^\dagger \hat{a}_{q, \sigma} | \tilde{\Psi}'_0 \rangle \\
&= \mathcal{E}'_0 + \sum_p (v_p - v'_p) n_p^{\tilde{\Psi}'_0}
\end{aligned} \tag{14}$$

and

$$\begin{aligned}
\langle \tilde{\Psi}_0 | \sum_{pq,\sigma=\alpha,\beta} h'_{pq} \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} + \hat{W}_{ee} | \tilde{\Psi}_0 \rangle &= \langle \tilde{\Psi}_0 | \sum_{pq,\sigma=\alpha,\beta} h_{pq} \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} + \hat{W}_{ee} | \tilde{\Psi}_0 \rangle \\
&+ \langle \tilde{\Psi}_0 | \sum_{pq,\sigma=\alpha,\beta} (h'_{pq} - h_{pq}) \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \tilde{\Psi}_0 \rangle \\
&= \mathcal{E}_0 + \sum_p (v'_p - v_p) n_p^{\tilde{\Psi}_0}.
\end{aligned} \tag{15}$$

By combining Eqs. (12)-(15) with the assumption $n_p^{\tilde{\Psi}'_0} = n_p^{\tilde{\Psi}_0} = n_p^0$ we finally obtain

$$\mathcal{E}_0 < \mathcal{E}'_0 + \sum_p (v_p - v'_p) n_p^0 \tag{16}$$

and

$$\mathcal{E}'_0 < \mathcal{E}_0 + \sum_p (v'_p - v_p) n_p^0. \tag{17}$$

Conclude.

We conclude from Eqs. (16) and (17) that, under our orbital occupation assumption,

$$0 < \mathcal{E}'_0 - \mathcal{E}_0 + \sum_p (v_p - v'_p) n_p^0 < 0, \tag{18}$$

which is absurd. In conclusion, there is a one-to-one correspondence between the diagonal one-electron integrals $\{v_p\}_p$ and the orbital occupations $\{n_p^{\tilde{\Psi}_0}\}_p$ in the ground-state seniority-zero wavefunction.

Why can this result be seen as a kind of Hohenberg–Kohn theorem for seniority-zero wavefunctions?

The collection of occupation numbers $\{n_p^{\tilde{\Psi}_0}\}_p$ can be seen as an electron density in the molecular orbital space. The density “on the orbital p ” is $n_p^{\tilde{\Psi}_0}$. Formally [see the energy expression in Eq. (11)], the collection of diagonal one-electron integrals $\{v_p\}_p$ looks like a potential, by analogy with DFT. The value of this potential “on the orbital p ” is v_p . In this respect, the theorem we proved is a Hohenberg–Kohn-like theorem.