Exam in Advanced Quantum Chemistry – M2 course

January 2025, Two-hour exam

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1. Essay [10 points]

Write a structured and concise essay on the topic "Electron correlation and Chemistry". *What is electron correlation? Why do chemists refer to different types of correlations in electronic structure theory? Quantum mechanics relies on a single fundamental equation, the Schrödinger equation. Nevertheless, there is a plethora of theories and methods in quantum chemistry. How is that possible?* These are the questions you are expected to address in your essay, with a particular focus on accuracy versus computational feasibility. You are encouraged to illustrate your prose with well-explained and enlightening equations.

2. Exercise: Quantum embedding of molecular fragments [13 points]

The present exercise is an intuitive introduction to *density matrix embedding theory* (DMET), a theory that was proposed in 2012 by Knizia and Chan *[Phys. Rev. Lett.* **109**, *186404 (2012)]* as an efficient strategy for computing large electronic systems "piece-by-piece". We will assume throughout the exercise that the full system under study is described at the Hartree–Fock (HF) level of approximation. ***Real algebra will be used.***

a) We denote $\{\varphi_I\}_{1\leq I\leq N}$ the orthonormal set of occupied canonical HF molecular spin-orbitals. The corresponding N-electron Slater determinant reads $|\Phi\rangle = \prod_{I=1}^{N} \hat{a}_I^\dagger |\text{vac}\rangle$ in second quantization. As further explained in the following, it is essential, in order to achieve the quantum embedding of a molecular fragment (i.e., a part of the full system), to use another orthonormal basis $\{\tilde{\varphi}_I\}_{1\leq I\leq N}$. The two bases are connected through a unitary transformation that reads as follows in second quantization,

$$|\Phi\rangle \equiv |\varphi_1\varphi_2\ldots\varphi_N| \quad \rightarrow \quad \left|\tilde{\Phi}\right\rangle \equiv |\tilde{\varphi}_1\tilde{\varphi}_2\ldots\tilde{\varphi}_N| = \prod_{I=1}^{N} \hat{a}_{\tilde{I}}^\dagger |\text{vac}\rangle = e^{-\hat{\kappa}} |\Phi\rangle \,, \tag{1}$$

where $\hat{\kappa} = \sum_{1\leq I<J}^{N} \kappa_{IJ} \left(\hat{a}_I^\dagger \hat{a}_J - \hat{a}_J^\dagger \hat{a}_I\right)$. **[1 pt]** Explain why $\hat{\kappa}|\Phi\rangle = 0$ and conclude that $\left|\tilde{\Phi}\right\rangle = |\Phi\rangle$. *We recall that* $e^{-\hat{\kappa}} = \sum_{p=0}^{+\infty} \frac{(-\hat{\kappa})^p}{p!}$.

b) We consider in the following an arbitrary fragment $\mathcal{F}$ of the full system, which is defined mathematically as the one-electron Hilbert subspace consisting of L_{frag} (where $L_{\text{frag}} << N$) orthonormal spin-orbitals, i.e., $\mathcal{F} = \left\{|\chi_F\rangle \equiv \hat{c}_F^\dagger |\text{vac}\rangle\right\}_{1\leq F\leq L_{\text{frag}}}$, these spin-orbitals being essentially localized in the spatial region of that fragment. The remaining localized spin-orbitals $\{|\chi_E\rangle\}_{E>L_{\text{frag}}}$ span the fragment's environment, i.e., the rest of the system. The (one-electron reduced) density matrix elements *in the localized spin-orbital basis* read $D_{PQ} = \left\langle \tilde{\Phi}\middle|\hat{c}_P^\dagger \hat{c}_Q\middle|\tilde{\Phi}\right\rangle$, where $\hat{c}_P^\dagger = \sum_{I=1}^{N} \langle\tilde{\varphi}_I|\chi_P\rangle\, \hat{a}_{\tilde{I}}^\dagger$ and $\hat{c}_Q = \sum_{J=1}^{N} \langle\tilde{\varphi}_J|\chi_Q\rangle\, \hat{a}_{\tilde{J}}$. **[1 pt]** Show that

$$D_{PQ} = \sum_{I=1}^{N} \langle\tilde{\varphi}_I|\chi_P\rangle \langle\tilde{\varphi}_I|\chi_Q\rangle \,. \tag{2}$$

c) We now define explicitly the first $L_{\rm frag}$ rotated occupied spin-orbitals $\{\tilde{\varphi}_I\}_{1\leq I\leq L_{\rm frag}}$ by projecting the fragment spin-orbitals onto the complete space of occupied HF spin-orbitals,

$$|u_F\rangle \underset{1\leq F\leq L_{\rm frag}}{=} \hat{\mathcal{P}}_{\rm occ}\,|\chi_F\rangle\,, \quad \text{where} \quad \hat{\mathcal{P}}_{\rm occ} = \sum_{I=1}^{N} |\tilde{\varphi}_I\rangle\,\langle\tilde{\varphi}_I| = \sum_{I=1}^{N} |\varphi_I\rangle\,\langle\varphi_I|\,, \tag{3}$$

and orthonormalizing the projections, thus leading to

$$|\tilde{\varphi}_I\rangle \underset{1\leq I\leq L_{\rm frag}}{=} \sum_{F=1}^{L_{\rm frag}} \left[\mathbf{S}^{-1/2}\right]_{IF} |u_F\rangle\,, \tag{4}$$

where the $L_{\rm frag}\times L_{\rm frag}$ overlap matrix $\mathbf{S}$ is defined through its elements as follows, $[\mathbf{S}]_{FF'} = \langle u_F|u_{F'}\rangle$. **[2 pts]** Show that the projector onto the corresponding "fragment occupied" subspace $\hat{\mathcal{F}}_{\rm occ} = \sum_{I=1}^{L_{\rm frag}} |\tilde{\varphi}_I\rangle\,\langle\tilde{\varphi}_I|$ reads

$$\hat{\mathcal{F}}_{\rm occ} = \sum_{F=1}^{L_{\rm frag}}\sum_{F'=1}^{L_{\rm frag}} \left[\mathbf{S}^{-1}\right]_{FF'} |u_F\rangle\,\langle u_{F'}|\,, \tag{5}$$

and check that $\hat{\mathcal{F}}_{\rm occ}\,|u_G\rangle = |u_G\rangle$, $1\leq G\leq L_{\rm frag}$. *We recall that the elements of the matrix product* $\mathbf{AB}$ *of two real Hermitian matrices* $\mathbf{A}$ *and* $\mathbf{B}$ *are evaluated as follows,* $[\mathbf{AB}]_{FF'} = \sum_I [\mathbf{A}]_{FI}\,[\mathbf{B}]_{IF'} = \sum_I [\mathbf{A}]_{IF}\,[\mathbf{B}]_{IF'}$.

d) **[1 pt]** Show that the overlap $\langle\tilde{\varphi}_I|\chi_F\rangle$ between a rotated occupied spin-orbital $\tilde{\varphi}_I$ ($1\leq I\leq N$) and a fragment one χ_F ($1\leq F\leq L_{\rm frag}$) can be written equivalently as follows, $\langle\tilde{\varphi}_I|\chi_F\rangle = \langle\tilde{\varphi}_I|u_F\rangle$. *For that purpose, use Eq. (3), and the fact that* $|\tilde{\varphi}_I\rangle = \hat{\mathcal{P}}_{\rm occ}\,|\tilde{\varphi}_I\rangle$ *and* $\hat{\mathcal{P}}_{\rm occ}$ *is Hermitian.*

e) **[2 pts]** The projection operator $\hat{\mathcal{P}}_{\rm core} = \sum_{I>L_{\rm frag}}^{N} |\tilde{\varphi}_I\rangle\,\langle\tilde{\varphi}_I|$ onto the complementary part of the occupied spin-orbital space (the so-called "core" subspace) is simply determined as follows, $\hat{\mathcal{P}}_{\rm core} = \hat{\mathcal{P}}_{\rm occ} - \hat{\mathcal{F}}_{\rm occ}$. Deduce from questions 2. c) and d) that the core and fragment spin-orbitals do not overlap, i.e., $\langle\tilde{\varphi}_I|\chi_F\rangle \underset{L_{\rm frag}<I\leq N}{=} \left\langle\tilde{\varphi}_I\middle|\hat{\mathcal{P}}_{\rm core}\middle|u_F\right\rangle = 0$. *For that purpose, use the fact that* $|\tilde{\varphi}_I\rangle \underset{L_{\rm frag}<I\leq N}{=} \hat{\mathcal{P}}_{\rm core}\,|\tilde{\varphi}_I\rangle$, $\hat{\mathcal{P}}_{\rm core}$ *is Hermitian, and* $\hat{\mathcal{P}}_{\rm occ}^2 = \hat{\mathcal{P}}_{\rm occ}$.

f) **[3 pts]** Deduce from questions 2. b) and e) that the density matrix elements involving at least one fragment spin-orbital index F can be evaluated exactly from the $L_{\rm frag}$-electron Slater determinant $\left|\tilde{\Phi}_{\rm cluster}\right\rangle = \prod_{I=1}^{L_{\rm frag}} \hat{a}_I^\dagger\,|{\rm vac}\rangle$ as follows, $D_{FQ} \underset{1\leq F\leq L_{\rm frag}}{=} \sum_{I=1}^{L_{\rm frag}} \langle\tilde{\varphi}_I|\chi_F\rangle\,\langle\tilde{\varphi}_I|\chi_Q\rangle = \left\langle\tilde{\Phi}_{\rm cluster}\middle|\hat{c}_F^\dagger\hat{c}_Q\middle|\tilde{\Phi}_{\rm cluster}\right\rangle$. Why is this a remarkable result? Why are $\{\tilde{\varphi}_I\}_{L_{\rm frag}<I\leq N}$ referred to as core spin-orbitals?

g) **[BONUS]** In order to determine variationally the "fragment occupied" spin-orbitals $\{\tilde{\varphi}_I\}_{1\leq I\leq L_{\rm frag}}$, we can distribute the "active" $L_{\rm frag}$ electrons among the $L_{\rm frag}$ spin-orbitals of the fragment $\mathcal{F}$ plus the $L_{\rm frag}$ orthonormalized (so-called *bath*) spin-orbitals $\left\{\tilde{\psi}_B\right\}_{1\leq B\leq L_{\rm frag}}$ that are obtained by projection (and orthonormalization) onto the fragment's environment (see question 2. b)), i.e., $\left|\tilde{\psi}_B\right\rangle \underset{1\leq B\leq L_{\rm frag}}{=} \sum_{F=1}^{L_{\rm frag}} \left[\mathbf{B}^{-1/2}\right]_{BF} |v_F\rangle$, where $[\mathbf{B}]_{FF'} = \langle v_F|v_{F'}\rangle$ and $|v_F\rangle = \sum_{E>L_{\rm frag}}^{N} \langle\chi_E|u_F\rangle\,|\chi_E\rangle$. The resulting $2L_{\rm frag}$-dimensional "fragment+bath" spin-orbital space is referred to as *embedding cluster*. **[3 pts]** Show that, according to Eqs. (2) and (3), the bath spin-orbitals can be determined directly from the density matrix as follows, $|v_F\rangle = \sum_{E>L_{\rm frag}}^{N} D_{EF}\,|\chi_E\rangle$. Check that the bath is orthogonal to the core, i.e., $\langle\tilde{\varphi}_I|v_F\rangle \underset{L_{\rm frag}<I\leq N}{=} 0$. *For that purpose, use the alternative expression* $|v_F\rangle = |u_F\rangle - \sum_{F'=1}^{L_{\rm frag}} \langle\chi_{F'}|u_F\rangle\,|\chi_{F'}\rangle$ *with questions 2. d) and e).* How could the present embedding scheme be exploited for performing (approximate) large-scale correlated computations?