Closed-shell parametrization

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1 Notation

1.1 Excitation operators

Let $\hat{a}^\dagger_{p,\sigma}(\hat{a}_{p,\sigma})$ be the creation (annihilation) operator associated with a spin-orbital

$$\psi_p(\mathbf{x}) \equiv \phi_p(\mathbf{r}) \otimes \sigma(m_s), \tag{1}$$

where $\phi_p(\mathbf{r})$ is a spatial orbitals, and $\sigma(m_s)$ a spin eigenfunction. The spin functions are orthonormal in the sense

$$\int \sigma^*(m_s)\tau(m_s)dm_s = \delta_{\sigma,\tau}. \tag{2}$$

Following Helgaker et al. [1], the singlet excitation operators are defined as

$$\hat{E}_{pq} \equiv \hat{a}^\dagger_{p,\alpha}\hat{a}_{q,\alpha} + \hat{a}^\dagger_{p,\beta}\hat{a}_{q,\beta}, \tag{3}$$

and satisfy the commutation relations

$$[\hat{E}_{pq}, \hat{E}_{rs}] = \hat{E}_{ps}\delta_{rq} - \hat{E}_{rq}\delta_{ps}. \tag{4}$$

Moreover, we introduce the two-electron excitation operator

$$\hat{e}_{pqrs} \equiv \hat{E}_{pr}\hat{E}_{qs} - \delta_{rq}\hat{E}_{ps} = \sum_{\sigma\tau} \hat{a}^\dagger_{p,\sigma}\hat{a}^\dagger_{q,\tau}\hat{a}_{s,\tau}\hat{a}_{r,\sigma}, \tag{5}$$

which satisfy the following commutation relation with $\hat{E}_{t,u}$

$$[\hat{e}_{pqrs}, \hat{E}_{tu}] = \hat{e}_{pqru}\delta_{ts} - \hat{e}_{ptrs}\delta_{qu} + \hat{e}_{pqus}\delta_{tr} - \hat{e}_{tqrs}\delta_{pu}. \tag{6}$$

1.2 The Hamiltonian

The second quantized representation of a nonrelativistic spin-free Hamiltonian containing at most two-particle interactions can now be written in terms of singlet and two-electron excitation operators as

$$\hat{H} = \sum_{pq} h^p_q \hat{E}_{pq} + \frac{1}{2}\sum_{pqrs} u^{pq}_{rs}\hat{e}_{pqrs}, \tag{7}$$

where the one- and two-body matrix elements h_q^p and u_{rs}^{pq} (physicist notation) are defined as

$$h_q^p \equiv \int \phi_p^*(\mathbf{r}) \hat{h} \phi_q(\mathbf{r}) d\mathbf{r}, \tag{8}$$

$$u_{rs}^{pq} \equiv \iint \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \hat{w}(\mathbf{r}_1, \mathbf{r}_2) \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{9}$$

where $\hat{h}$ is a one-body operator and $\hat{w}(\mathbf{r}_1, \mathbf{r}_2)$ is a two-particle interaction/operator (typically the electron-electron Coulomb interaction).

The expectation value of the (spin-free) Hamiltonian for a (closed-shell) reference determinant (usually the Hartree-Fock determinant) is given by

$$E_{\text{ref}} \equiv \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = 2 \sum_i h_i^i + 2 \sum_{ij} u_{ij}^{ij} - \sum_{ij} u_{ji}^{ij}, \tag{10}$$

where i, j run over all (doubly) occupied orbitals $\{\phi_i(\mathbf{r})\}_{i=1}^{N_{\text{docc}}}$. More generally, the expectation value of the Hamiltonian (or some other one- plus two-body operator) where $\langle \tilde{\Psi} |, |\Psi \rangle$ are (possibly independent) bra and ket states can be written as

$$\langle \tilde{\Psi} | \hat{H} | \Psi \rangle = \sum_{pq} h_q^p \gamma_p^q + \frac{1}{2} \sum_{pqrs} u_{rs}^{pq} \Gamma_{pq}^{rs}, \tag{11}$$

where we have defined the one- and two-body reduced density matrices

$$\gamma_p^q \equiv \langle \tilde{\Psi} | \hat{E}_{pq} | \Psi \rangle, \tag{12}$$

$$\Gamma_{pq}^{rs} \equiv \langle \tilde{\Psi} | \hat{e}_{pqrs} | \Psi \rangle. \tag{13}$$

The expressions for the reduced density matrices depend on the particular wavefunction parametrization used, i.e., Hartree-Fock, configuration interaction, coupled cluster, and approximate coupled cluster methods such as CC2 or OMP2.

1.3 Singlet configuration state functions

Single and double excited (ket/bra) (singlet) configuration state functions (CSFs) are defined as

$$|\Phi_i^a\rangle \equiv \hat{X}_i^a |\Phi_0\rangle, \quad |\Phi_{ij}^{ab}\rangle \equiv \hat{X}_{ij}^{ab} |\Phi_0\rangle, \tag{14}$$

$$\langle \Phi_i^a | \equiv \langle \Phi_0 | E_{ia}, \quad \langle \Phi_{ij}^{ab} | \equiv \langle \Phi_0 | E_{jb} E_{ia}, \tag{15}$$

where we have defined the single and double excitation (de-excitation) operators

$$\hat{X}_i^a \equiv \hat{E}_{ai}, \quad \hat{X}_{ij}^{ab} \equiv \hat{E}_{ai} \hat{E}_{bj}, \tag{16}$$

$$(\hat{X}_i^a)^\dagger = \hat{E}_{ia}, \quad (\hat{X}_{ij}^{ab})^\dagger = \hat{E}_{jb} \hat{E}_{ia}. \tag{17}$$

The CSFs defined this way are not orthogonal, and the overlaps are given by

$$\langle \Phi_i^a | \Phi_j^b \rangle = 2 \delta_{ab} \delta_{ij}, \tag{18}$$

$$\langle \Phi_{ij}^{ab} | \Phi_{kl}^{cd} \rangle = 2 \hat{P}_{ij}^{ab} \left(2 \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl} - \delta_{ac} \delta_{bd} \delta_{il} \delta_{jk} \right), \tag{19}$$

where we have defined the permutation operator

$$\hat{P}^{pq}_{rs} A^{pq}_{rs} = A^{pq}_{rs} + A^{qp}_{sr}. \tag{20}$$

However, following Refs. [1, 2] a biorthogonal basis can be defined (for singles and doubles), such that,

$$\langle \tilde{\Phi}^a_i | \Phi^c_k \rangle = \delta_{ac}\delta_{ik}, \tag{21}$$

$$\langle \tilde{\Phi}^{ab}_{ij} | \Phi^{cd}_{kl} \rangle = P^{ab}_{ij}\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl}, \tag{22}$$

by choosing

$$\langle \tilde{\Phi}^a_i | = \frac{1}{2} \langle \Phi^a_i | = \langle \Phi_0 | \hat{Y}^i_a, \tag{23}$$

$$\langle \tilde{\Phi}^{ab}_{ij} | = \frac{1}{3} \langle \Phi^{ab}_{ij} | + \frac{1}{6} \langle \Phi^{ab}_{ji} | = \langle \Phi_0 | \hat{Y}^{ij}_{ab}, \tag{24}$$

where we have defined the single and double de-exciation operators

$$\hat{Y}^i_a = \frac{1}{2}\hat{E}_{ia}, \tag{25}$$

$$\hat{Y}^{ij}_{ab} = \frac{1}{3}\hat{E}_{jb}\hat{E}_{ia} + \frac{1}{6}\hat{E}_{ib}\hat{E}_{ja} \tag{26}$$

2 Configuration interaction

2.1 CISD

We use the following parametrization of the CISD ket and bra wavefunction

$$|\Psi\rangle = C_0 |\Phi_0\rangle + \sum_{ai} C^a_i |\Phi^a_i\rangle + \frac{1}{2}\sum_{abij} C^{ab}_{ij} |\Phi^{ab}_{ij}\rangle, \tag{27}$$

$$\langle \tilde{\Psi}| = \langle \tilde{\Phi}_0 | \tilde{C}_0 + \sum_{ia} \tilde{\Phi}^a_i \tilde{C}^i_a + \frac{1}{2}\sum_{ijab} \langle \tilde{\Phi}^{ab}_{ij} | \tilde{C}^{ij}_{ab}, \tag{28}$$

where the left expansion coefficients $\tilde{C}$ are related to the right coefficients C by

$$\tilde{C}_0 = C^*_0, \tag{29}$$

$$\tilde{C}^i_a = 2C^{a*}_i, \tag{30}$$

$$\tilde{C}^{ij}_{ab} = \left(4C^{ab}_{ij} - 2C^{ab}_{ji}\right)^*, \tag{31}$$

and the doubles coefficients satisfy the symmetry relation

$$C^{ab}_{ij} = C^{ba}_{ji}, \tag{32}$$

$$\tilde{C}^{ij}_{ab} = \tilde{C}^{ji}_{ba}. \tag{33}$$

The norm/overlap of the bra and ket states is given by

$$\langle\tilde{\Psi}|\Psi\rangle = \tilde{C}_0 C_0 + \sum_{ai} \tilde{C}^i_a C^a_i + \frac{1}{2}\sum_{abij} \tilde{C}^{ij}_{ab} C^{ab}_{ij}, \tag{34}$$

Right and left sigma-vectors are defined as

$$\sigma_\mu \equiv \sum_\nu \langle\tilde{\Phi}_\mu|\hat{H}|\Phi_\nu\rangle\, C_\nu, \tag{35}$$

$$\tilde{\sigma}_\nu \equiv \sum_\mu \tilde{C}_\mu\, \langle\tilde{\Phi}_\mu|\hat{H}|\Phi_\nu\rangle\,. \tag{36}$$

Working equations/algebraic expressions for the (closed-shell) sigma-vectors and the one- and two-body density matrices can be generated symbolically with the `drudge/gristmill` package [3, 4].

The CIS and CID approximation are obtained by setting the doubles or singles coefficients to zero, respectively.

3 Coupled cluster

3.1 CCSD

The right and left CCSD wavefunctions are parametrized as

$$|\Psi\rangle = e^{\hat{T}}\,|\Phi_0\rangle\,, \quad \langle\tilde{\Psi}| = \langle\Phi_0|\left(1+\hat{\Lambda}\right)e^{-\hat{T}}, \tag{37}$$

where we have defined the cluster excitation (de-excitation) operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2, \quad \hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 \tag{38}$$

$$\hat{T}_1 = \sum_{ai} \tau^a_i \hat{X}^a_i, \quad \hat{T}_2 = \frac{1}{2}\sum_{abij} \tau^{ab}_{ij} \hat{X}^{ab}_{ij}, \tag{39}$$

$$\hat{\Lambda}_1 = \sum_{ia} \lambda^i_a \hat{Y}^i_a, \quad \hat{\Lambda}_2 = \frac{1}{2}\sum_{ijab} \lambda^{ij}_{ab} \hat{Y}^{ij}_{ab}, \tag{40}$$

and the CCSD energy functional is given by

$$\mathcal{H} = \langle\tilde{\Psi}|\hat{H}|\Psi\rangle\,. \tag{41}$$

Similar to CISD, the doubles amplitudes satisfy the symmetry relation

$$\tau^{ab}_{ij} = \tau^{ba}_{ji}, \tag{42}$$

$$\lambda^{ij}_{ab} = \lambda^{ji}_{ba}. \tag{43}$$

The CCSD-amplitudes (λ, τ) (for the ground state) are determined by solving the (non-linear) amplitude equations

$$\frac{\partial\mathcal{H}}{\partial\lambda_\mu} = \langle\Phi_0|\hat{Y}^\mu e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0, \tag{44}$$

$$\frac{\partial\mathcal{H}}{\partial\tau^\mu} = \langle\Phi_0|\left(1+\hat{\Lambda}\right)e^{-\hat{T}}[\hat{H}, \hat{X}_\mu]e^{\hat{T}}|\Phi_0\rangle = 0, \tag{45}$$

where μ denotes the excitation level (singles or doubles).

$$\gamma_p^q \equiv \langle \tilde{\Psi} | \hat{E}_{pq} | \Psi \rangle \,, \tag{46}$$

$$\Gamma_{pq}^{rs} \equiv \langle \tilde{\Psi} | \hat{e}_{pqrs} | \Psi \rangle \tag{47}$$

Excited states can be determined with the EOM-CCSD approach, where the left and right excited states are parametrized as

$$|\Psi_k\rangle = \hat{R}_k e^{\hat{T}} \, |\Phi_0\rangle \,, \tag{48}$$

$$\langle \tilde{\Psi}_k | = \langle \tilde{\Phi}_0 | \, \hat{L}_k e^{-\hat{T}}, \tag{49}$$

where

$$\hat{R}_k = \sum_{\mu=0} r_k^\mu \hat{X}_\mu, \quad \hat{L}_k = \sum_{\mu=0} l_{k,\mu} \hat{Y}^\mu. \tag{50}$$

The EOM coefficients l, r are determined by solving the left and right eigenvalue problems

$$\sigma_\mu = E_k r_k^\mu, \tag{51}$$

$$\tilde{\sigma}_\nu = E_k l_{\nu,k} \tag{52}$$

where we have defined the EOM sigma-vectors

$$\sum_\nu \bar{H}_{\mu,\nu} r_k^\nu \equiv \sigma_\mu, \tag{53}$$

$$\sum_\mu l_{k,\mu} \bar{H}_{\mu,\nu} \equiv \tilde{\sigma}_\nu, \tag{54}$$

and the matrix elements of the similarity transformed Hamiltonian $\bar{H} \equiv e^{-\hat{T}} \hat{H} e^{\hat{T}}$

$$\bar{H}_{\mu,\nu} \equiv \langle \Phi_\mu | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_\nu \rangle \,. \tag{55}$$

Moreover, the right and left eigenvectors can be normalized such that they form a bi-orthonormal set, i.e.,

$$\langle \tilde{\Psi}_k | \Psi_l \rangle = \delta_{k,l}. \tag{56}$$

Working equations for the (closed-shell) amplitude equations and the sigma vectors can be generated with the `drudge/gristmill` package.

References

[1] T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular electronic-structure theory* (John Wiley & Sons, 2013).

[2] P. Pulay, S. Saebo/, and W. Meyer, "An efficient reformulation of the closed-shell self-consistent electron pair theory", The Journal of chemical physics **81**, 1901–1905 (1984).

[3]J. Zhao, G. P. Chen, G. Harsha, M. Wholey, T. M. Henderson, and G. E. Scuseria, *Drudge: a symbolic algebra system for tensorial and noncommutative algebras*, GitHub repository, 2016–2025.

[4]J. Zhao, "Symbolic solution for computational quantum many-body theory development", PhD thesis (Rice University, Houston, Texas, USA, Apr. 2018).