

A 10 Modern Electron Correlation Methods in Quantum Chemistry

Th. Müller

Zentralinstitut für Angewandte Mathematik

Forschungszentrum Jülich GmbH

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1 Introduction

The term electron correlation methods in Quantum Chemistry comprises all methods that go beyond the simple mean-field Hartree-Fock (HF) Self-Consistent Field model. The electronic wavefunction which depends on the coordinates of N electrons is approximated in terms of a Slater determinant, i.e., the antisymmetrized product of N spin-orbitals $\phi(\mathbf{r}, \sigma)$ (one-electron functions). Expanding these orbitals in terms of a limited number of spatial basis functions times a spin function and fully optimizing the coefficients as to minimize the total electronic energy within a given nuclear framework defines the HF method.

In the statistical sense uncorrelated electrons imply that the probability density $P(r_1, r_2)$ of finding two electrons 1 and 2 *simultaneously* at positions r_1 and r_2 , respectively, is given by a product of one-electron densities $P(r)$

$$P(r_1, r_2) = \gamma P(r_1)P(r_2) = \frac{N-1}{N} P(r_1)P(r_2) \quad (1)$$

where γ is the renormalization factor [1]. The antisymmetry constraint imposed upon the wavefunction by the Pauli principle causes the HF model to incorporate electron correlation between electron pairs of alike spin (Fermi correlation). Pairs of electrons with opposite spin, however, are not correlated (Coulomb correlation).

Approximating the electronic wavefunction by a single Slater determinant, disregarding the effect of basis-set truncation, is a serious constraint and may result in a qualitatively incorrect description of the wavefunction as compared to the exact solution. This is particularly apparent in case of molecular dissociation into open-shell fragments which cannot be described properly in terms of a single (closed-shell) Slater determinant. In Chemistry primarily energy differences are of interest. Nevertheless, aiming at the so-called *chemical accuracy* of 1kcal/mol it is essential to quantitatively account for *differential* electron correlation effects. This is the realm of modern electron correlation methods.

Subsequently the basic concepts are described, followed by sketching some widely used multi- and single-reference electron correlation methods. Electron correlation is discussed here in terms of one- and N-electron basis set expansions, rather than in terms of a physical interpretation. Density Functional Theory is explicitly excluded as it is conceptionally completely different and well-covered in other chapters of this book.

2 Basic concepts

2.1 Hamiltonian

The standard molecular Hamiltonian used in electronic structure calculations in atomic units contains the electronic kinetic energy \mathcal{T}_e , electron-electron repulsion \mathcal{V}_{ee} , electron-nuclei attraction \mathcal{V}_{ne} and the nuclear-nuclear repulsion energy V_{nn} and runs

$$\begin{aligned} \mathcal{H} &= -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iA} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{A>B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \\ &= \mathcal{T}_e + \mathcal{V}_{ee} + \mathcal{V}_{ne} + V_{nn}. \end{aligned} \quad (2)$$

Z denotes the nuclear charge, \mathbf{R} and \mathbf{r} are nuclear and electronic position vectors, respectively. Summations run over all electrons (index i, j) and nuclei (index A, B). This equation implies

several simplifications: (i) the particles interact non-relativistically solely through Coulombic interaction (ii) the (clamped-nucleus) Born-Oppenheimer Approximation and (iii) the particles are described as point charges neglecting the finite size of the nuclei.

Relativistic contributions to the total energy, which scale as Z^4/c^2 with c the speed of light (≈ 137 a.u.), must be included for the heavier elements in at least some approximate manner (e.g. relativistic effective core potentials [2, 3], scalar relativistic effects). The impact of spin-orbit coupling may be of similar importance as electron correlation for the heavier elements and cannot be straightforwardly ignored.

The Born-Oppenheimer approximation [4, 5], sometimes referred to as *adiabatic* approximation [6], decouples electron motion from the motion of the nuclei. It works well wherever the gradient of the electronic wavefunction with respect to the nuclear coordinates is small. This assumption may be violated close to avoided crossings between different electronic states where the characteristics of the participating states rapidly change. Proper treatment of these regions, which are of great importance for the understanding of the dynamics of photochemical reactions, invariably require the inclusion of *non-adiabatic* coupling terms [7].

2.2 Wave function expansion

The eigenvalues and eigenfunctions of the time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \quad (4)$$

are sought. As analytical solutions are unavailable except for the one-electron case an expansion in an N-particle basis set $\{\Phi\}$ offers a solution. For an initial trial wavefunction $\hat{\Psi}(\alpha)$ which depends on a set of parameters $\{\alpha\}$ the energy functional runs

$$\hat{E}(\alpha) = \frac{\langle \hat{\Psi}(\alpha) | \mathcal{H} | \hat{\Psi}(\alpha) \rangle}{\langle \hat{\Psi}(\alpha) | \hat{\Psi}(\alpha) \rangle}. \quad (5)$$

By virtue of the variation theorem the approximation $\hat{E}(\alpha)$ is an upper bound to the exact energy of eqn. 4 and the wavefunction $\hat{\Psi}(\alpha)$ will converge on average to the exact wavefunction Ψ .

Using a linear expansion in terms of α

$$\Psi = \sum_i \alpha_i \Phi_i \quad (6)$$

a generalized eigenvalue problem results from making the energy stationary with respect to α

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (7)$$

$$\mathbf{H}_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle \quad (8)$$

$$\mathbf{S}_{ij} = \langle \Phi_i | \Phi_j \rangle \quad (9)$$

\mathbf{H}_{ij} and \mathbf{S}_{ij} denote the hamiltonian and overlap matrix elements with respect to the basis functions Φ_i and Φ_j . The Dirac notation implies $\langle \Phi_i | \mathcal{O} | \Phi_j \rangle = \int \Phi_i^* \mathcal{O} \Phi_j d\tau$. As the N-particle basis is usually chosen orthonormal, the overlap matrix is replaced by the unit matrix. For a complete N-particle basis set this approach yields the exact solution of eqn. 4. However, such a basis would be infinite in size and rather impractical to use.

Practical guidelines for the construction of the N-particle basis are the efficient representation of the N-particle space and the rapid evaluation of the respective matrix elements, i.e., the computation of a vast number of multi-dimensional N-electron integrals appearing in eqn. 8. Conventionally, the N-electron basis is constructed from antisymmetrized products of orthonormal spinorbitals $\phi_{ki}(\mathbf{r}_i)$, denoted Slater determinants Φ .

$$\Phi_i = \mathcal{A} \prod_k^N \phi_{ki}(\mathbf{r}_i) \quad (10)$$

The spinorbitals $\phi_{ki}(\mathbf{r}_i)$ are in turn constructed from linear combinations of spatial atom-centered one-electron basis functions χ_μ times a spin function σ . The favourable mathematical properties of Gaussian Type Orbitals (GTOs) for integral evaluation make them the preferred choice for $\chi_\mu(\mathbf{r})$.

$$\phi_i = \sigma_i \sum_{\mu} C_{\mu i} \chi_{\mu}(\mathbf{r}_i) = \sigma_i \tilde{\phi}_i \quad (11)$$

$$\chi_{\mu}(\mathbf{r}) = x^{l_{\mu}} y^{m_{\mu}} z^{n_{\mu}} e^{-\alpha_{\mu} r^2} \quad (12)$$

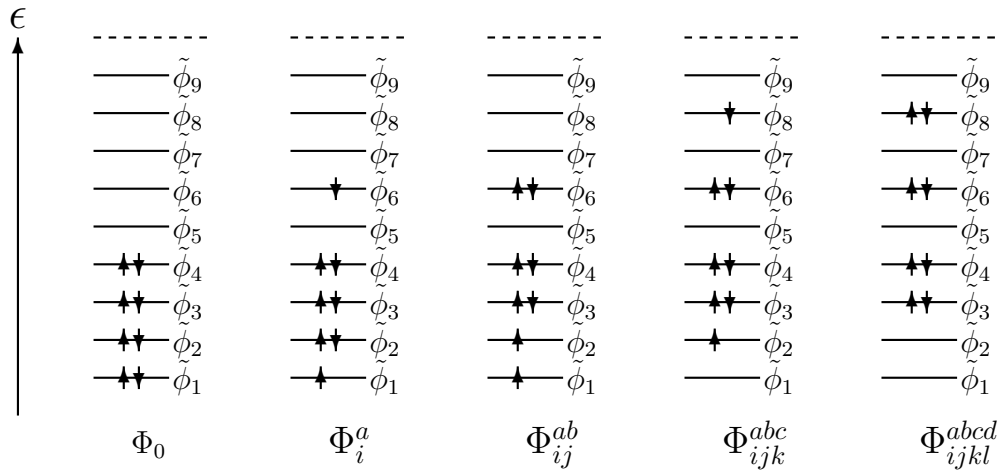


Fig. 1: Schematic construction of closed-shell ground-state (Φ_0), singly (Φ_i^a), doubly (Φ_{ij}^{ab}), triply (Φ_{ijk}^{abc}) and quadruply (Φ_{ijkl}^{abcd}) excited determinants.

Fig. 1 schematically depicts the construction of the N-particle basis set. The spatial orbital coefficients $C_{\mu i}$ (molecular orbital coefficients) are usually obtained from HF or MCSCF wavefunction optimizations. The molecular orbitals (MOs) $\{\tilde{\phi}\}$ are ordered according to their eigenvalues (orbital energies ϵ). The ground (or reference) state is constructed by filling the energetically lowest-lying orbitals with electrons. Singly, doubly, triply and quadruply excited determinants are obtained by "exciting" electrons from some occupied orbitals in the reference state to unoccupied orbitals. Continuing up to N-fold excitations generates the full N-particle basis. Slater determinants are in general no eigenfunctions to S^2 . This gives potentially rise to spin-contamination problems. However, spin-adapted configurations (CSFs) may be constructed by taking the appropriate linear combinations of Slater determinants.

Since a molecule is built from atoms and the chemical binding energy is much smaller than the total electronic energy of the individual atoms this choice of atom centered basis functions

allows for a compact representation of the electronic wavefunction. The *Restricted* Hartree-Fock (RHF) model constraints each MO to be doubly occupied so that pairs of spin-orbitals with unlike spin share the same spatial function. This constraint is lifted in the *spin-polarized* or *unrestricted* HF method. Hence, UHF calculations yield in general no eigenfunctions of S^2 and thereby give rise to unphysical solutions of the Schrödinger equations. The additional flexibility, however, allows UHF to include some Coulomb correlation. PUHF calculations correspond to their UHF counterparts with the undesired contamination by higher multiplicities is approximately removed by projection.

The atom-centered basis sets $\{\chi\}$ are composed of sets of atom-specific GTOs with their free parameters $l_\mu, m_\mu, n_\mu, \alpha_\mu$ optimized by HF and/or electron correlation methods as to minimize the total energy for the ground state or an average of several low-lying excited states. For efficiency reasons instead of using primitive GTOs, fixed linear combinations of primitive GTOs located on one center (CGTOs) are used. It is advisable to use systematically constructed basis set sequences so that switching to larger basis sets yields a balanced and uniform improvement of the one-electron basis. This property forms the basis for the extrapolation of the computed properties to the limit of a complete basis set $\{\chi\}$. Popular basis sets with this property are e.g. *atomic natural orbitals* (ANO) [8, 9] and *correlation consistent basis sets* (cc-pVXZ, cc-pCVXZ X=D,T,Q,5,6)[10]. Many basis sets are available from <http://www.emsl.pnl.gov/forms/basisform.html>. For electron correlation methods basis sets of triple zeta quality are the minimum requirement - smaller basis sets are not flexible enough to describe electron correlation reasonably well.

The number of CSFs that can be constructed from n molecular orbitals and N electrons subject to a spin-multiplicity of $S = b/2$ [11] is given by:

$$N_{csf} = \frac{b+1}{n+1} \binom{n+1}{a} \binom{n+1}{n-a-b} \quad \text{where } N = 2a + b \quad S = b/2 \quad (13)$$

Table 1 collects some representative numbers for the size of a full N-particle basis for singlet states ($S = 0$). The case $n = N$ corresponds typically to a basis set of cc-pVDZ quality, whereas $n = 2N$ comes close to cc-pVTZ quality basis sets suitable for electron correlation methods. Evidently, using the linear expansion of the wavefunction (eqn. 6) in terms of all possible CSFs in a given basis set $\{\phi\}$ (denoted full configuration interaction (FCI)) is ruled out by the *factorial* growth of the N-particle space, except for the very smallest systems with at most 10 to 20 electrons in small basis sets (see e.g. [12]). The truncation of the one- and

Table 1: Total size of the N-particle basis for singlet states as function of the number of electrons N and molecular orbitals n : $N_{csf} = \frac{1}{n+1} \binom{n+1}{N/2}^2$.

N	n=N N_{csf}	n=2N N_{csf}
4	20	336
8	1 764	866 320
12	226 512	3 405 278 800
16	34 763 300	16 226 413 117 200
20	5 924 217 936	86 391 974 193 251 584
24	1 081 724 803 600	494 452 245 428 329 102 096

N-particle basis are the most important errors in quantum chemical calculations.

2.3 Non-dynamical versus dynamical electron correlation

Truncating the N-electron wavefunction expansion to a single determinant and variational optimization of the remaining parameters, the MO coefficients, defines the Hartree-Fock method. Since the Hartree-Fock solution forms the basis for most advanced electron correlation methods, the electron correlation energy is defined as the difference between the exact non-relativistic energy and its HF counterpart in a *complete* basis $\{\Phi\}$:

$$E_{corr} = E_{exact} - E_{HF\infty} \quad (14)$$

By itself E_{exact} is ill-defined and must be obtained from experimental data corrected for relativistic effects. Considering electron correlation as the inadequacy of the N-electron wavefunction expansion in terms of a single Slater determinant (or a single CSF) by the HF method two different effects can be identified.

The HF wavefunction by itself may be even qualitatively incorrect because low-lying configurations strongly interact with each other resulting in large off-diagonal elements of \mathbf{H} (eqn. 7), so that the wavefunction is of *multi-configurational* nature. This effect is termed *non-dynamical* electron correlation. It is frequently of no importance for closed-shell molecules close to their equilibrium geometries but rapidly gains importance for open-shell systems, in excited states, transition metal compounds, for molecular systems at strained structures as well as a consequence of bond disruption or bond breaking.

Dynamical electron correlation arises because - even though qualitatively correct - the HF mean-field model cannot catch the instantaneous electron-electron interaction correctly. The mathematical structure of the Hamiltonian enforces Kato's cusp condition [13]: there is a singularity in the Hamiltonian close to the coalescence point where the interelectronic distance of a pair of electrons $|\mathbf{r}_i - \mathbf{r}_j| = r_{ij} \rightarrow 0$ vanishes. To cancel this singularity the wave function must contain linear terms r_{ij} so that there is a cusp at the coalescence point. To describe this cusp in terms of products one-electron functions requires high-angular momentum basis functions (angular correlation). Dynamical correlation effects may be accounted for by a variety of methods. Single-reference methods imply a qualitatively correct HF reference state whereas more general multi-reference methods can cope with any multi-configurational reference wavefunction.

3 Electron correlation methods

Electron correlation methods aim at approximating the FCI result, i.e., expanding the wavefunction in the full N-electron basis at a given one-electron basis set. Different methods can be classified by the way the FCI space is truncated. Fig. 2 schematically depicts the situation.

To account for non-dynamical electron correlation the most important spin-adapted configurations are included into the SCF procedure (multi-configurational SCF (MCSCF)). The coefficients of the CI expansion as well as the MO coefficients are optimized simultaneously. This requires an optimization of a non-linear function of *redundant* parameters so that the MCSCF method (cf. [14]) is more complex than HF and is occasionally plagued by convergence problems.

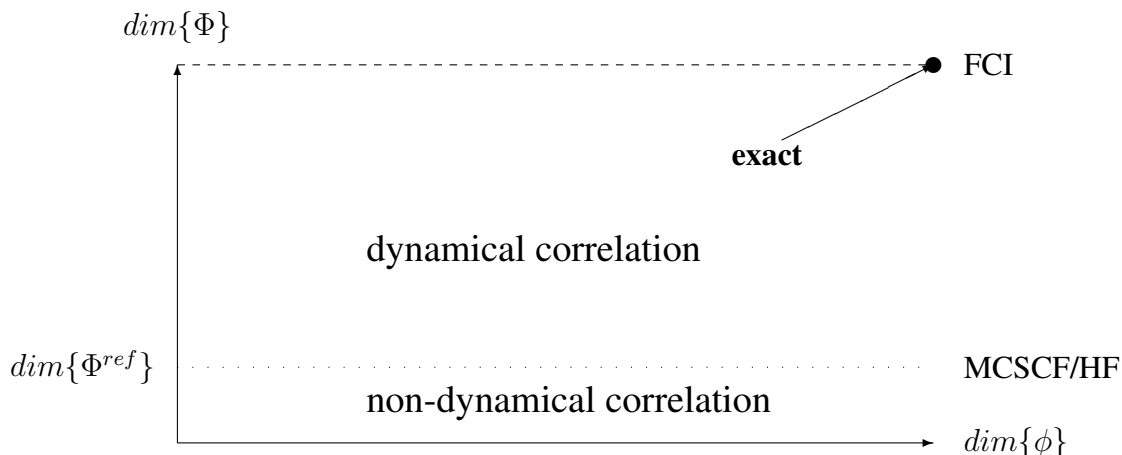


Fig. 2: Schematic representation of basis set truncation effects. The dotted line indicates the reference configuration space dimension and the dashed line the dimension of the FCI space. Given a fixed basis set $\{\phi\}$ various methods are points along a vertical line.

Electron correlation methods usually require the integrals in the $\{\phi\}$ basis. They are initially computed in the $\{\chi\}$ basis and must be transformed

$$\langle ij|ab\rangle = \sum_{\mu\nu\kappa\lambda} C_{\mu i} C_{\nu j} C_{\kappa a} C_{\lambda b} \langle \mu\nu|\kappa\lambda\rangle \quad (15)$$

$$\langle \mu\nu|\kappa\lambda\rangle = \int \chi_{\mu}(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_{\kappa}(\mathbf{r}_1) \chi_{\lambda}(\mathbf{r}_2) d\tau \quad (16)$$

which formally requires $O(n^8)$ floating point operations. Splitting it up into four separate partial summations it reduces to $O(4n^5)$. Further reductions occur for methods which require a subset of all integrals, only. Due to this AO-MO transformation of the integrals "non-local" electron correlation methods scale as $O(n^5)$ or worse.

3.1 Multi-configurational self consistent field (MCSCF)

To set up a MCSCF calculation the configuration space must be specified. This can become very tedious in case of large molecules or a complex bonding situation. Here the complete active space (CAS) approach and its modifications are fairly robust (cf. Fig. 3): specifying the number of active orbitals and electrons, a FCI expansion within this space is defined taking care of the non-dynamical electron correlation effects. Due to the factorial dependence of FCI expansions on the number of orbitals (cf. Table 1), CASSCF expansions are mostly limited to about 12 electrons in 12 orbitals (CASSCF(12,12)) corresponding to 226512 spin-adapted configurations for a singlet state. Consequently, restricted active space (RAS) expansions use a rather small RAS2 space along with typically at most 2 holes and electrons in RAS1 and RAS3, respectively (cf. Fig. 3). Such choice includes the most important electron correlation effects within RAS1 and RAS3 as well as the coupling between the subspaces. The choice of 1 hole and electron, respectively, corresponds to including polarization effects for coupling the RAS spaces. Thus, CASSCF and RASSCF calculations are usually limited by the size of the active space, which cannot be chosen arbitrary small in case, e.g., of transition metal compounds and

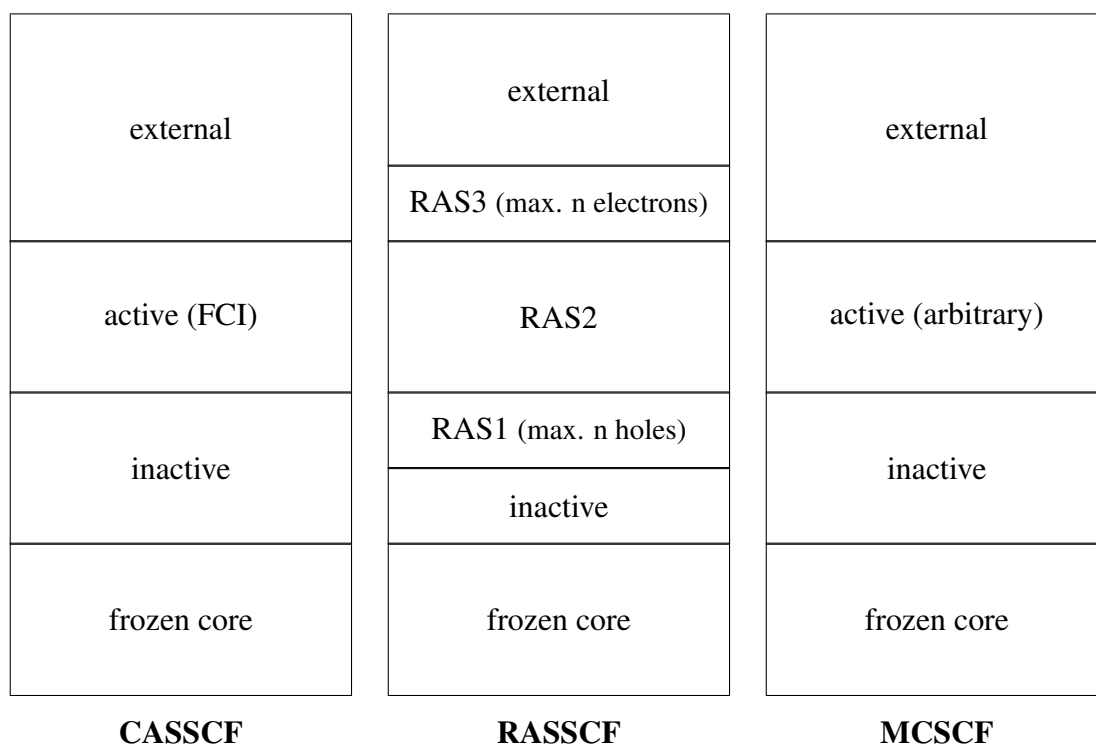


Fig. 3: Configuration and orbital space selection for non-dynamical electron correlation treatment. Frozen core orbitals remain unoptimized, inactive orbitals are kept doubly occupied, external orbitals are unoccupied throughout. For MCSCF calculations the configuration space in the active orbital subspace is arbitrary, CASSCF uses a FCI expansion, and RASSCF extends the active space by RAS1 orbitals kept doubly occupied with at most n holes and RAS3 orbitals kept empty except for at most n electrons and RAS2 accommodating a FCI expansion plus excitations from RAS1 to RAS2 and RAS2 to RAS3.

compounds with largely delocalized electrons. To set up these kind of calculations cannot be automated although there are practical guide lines that work in many cases. Yet, it is not a black box procedure.

In most cases MCSCF calculations do not provide even semi-quantitatively correct results due to the lack of dynamical electron correlation. They solely provide a qualitatively correct and well-balanced zeroth order description of wavefunction and are thus invariably followed by multi-reference configuration interaction or perturbation theory. Note, that the redundancy of CI and MO coefficients causes the MO coefficients to be not completely defined. This must be fixed prior to starting the separate dynamic electron correlation treatment by resolving the orbitals with the eigenvectors of the matrix representation of some operator (usually the one-electron density or a generalized Fock operator).

Occasionally it may be difficult to construct a configuration space yielding a qualitatively correct zeroth order wavefunction and thereby reasonably unbiased one-electron basis (MOs). It must be stressed that any optimization of the MO coefficients independent of the method results in bias towards the selected wavefunction expansion. As dynamical and non-dynamical electron correlation treatment constitute separate stages, it is very important to avoid an erroneous bias at the MCSCF level. Any substantial bias can be corrected for at the subsequent dynamical electron correlation treatment with large effort, only (e.g. [15]).

3.2 Møller-Plesset perturbation theory to nth Order (MPn)

The Hamilton operator is split into a reference \mathcal{H}_0 and a perturbation \mathcal{H}' . It is assumed that the unperturbed system can be solved with all eigenvalues and eigenvectors available while the perturbation is small in some sense. The standard procedure to derive Rayleigh-Schrödinger perturbation theory introduces an ordering parameter λ , expands the exact eigenvalues and eigenfunctions in a Taylor series in λ and inserts these terms into the Schrödinger equation. To hold for all values of λ one equation for each order is obtained. This finally yields in intermediate normalization, i.e., $\langle \Psi_0 | \Psi_0 \rangle = 1$

$$\Psi = \Psi_0 + \sum_i^n \Psi_i \quad (17)$$

$$E = \tilde{E}_0 + \sum_i^n \tilde{E}_i \quad (18)$$

$$\tilde{E}_n = \langle \Psi_0 | \mathcal{H}' | \Psi_{n-1} \rangle \quad (19)$$

The Møller-Plesset partitioning employs the effective one-electron Fock operator \mathcal{F} as \mathcal{H}_0 and the perturbation becomes the difference between \mathcal{H}_0 and the exact Hamilton operator (fluctuation potential). The zeroth order wavefunction is the HF wavefunction and the full set of eigenvectors and eigenvalues is given by all possible Slater determinants that can be constructed from $\{\phi\}$ and the sum of the energies of the occupied orbitals, respectively.

$$\mathcal{H}_0 = \sum_i^N \mathcal{F}_i, \quad \tilde{E}_0 = \sum_i^N \epsilon_i, \quad \Psi_0 = \Phi_0 \quad (20)$$

\tilde{E}_0 is *not* the HF energy. Adding the first order correction $\tilde{E}_1 = \langle \Psi_0 | \mathcal{H}' | \Psi_0 \rangle$ reproduces the HF energy. Expanding Ψ_1 in terms of the eigenvectors of \mathcal{H}_0 and reinserting into eqn. 19 finally yields \tilde{E}_2 in terms of two-electron integrals and orbital energies

$$\tilde{E}_2 = \sum_{i < j} \sum_{a < b} \frac{|\langle \Phi_{ij}^{ab} | \mathcal{H}' | \Phi_0 \rangle|^2}{\langle \Phi_{ij}^{ab} | \mathcal{H}_0 - E_0 | \Phi_{ij}^{ab} \rangle} = \sum_{i < j} \sum_{a < b} \frac{|\langle ij | ab \rangle - \langle ij | ba \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (21)$$

The computational cost for the evaluation of the MP2 energy is solely determined by the AO-MO integral transformation step. A variant thereof employing the resolution of identity approximation, which amounts to expanding orbital products in terms of a single atom centered auxiliary basis, succeeds in reducing the computational effort substantially compared to the standard approach though still of $O(n^5)$ albeit with a smaller prefactor [22].

MPn requires that the HF wavefunction is a good approximation to the fully perturbed system. Investigating the convergence properties of the series up to MP48 for H₂O and NH₂ [23] indicates that the MP series is rapidly convergent close to equilibrium geometries but either erratic (RHF reference) or extremely slowly convergent (UHF reference) away from the equilibrium. A study on Ne indicates [24], that even in this perfect single-reference case the MPn series may diverge(!) if the basis set contains diffuse functions. In practice the MPn series to low order does not show a monotonic convergence and going to higher orders, it will presumably often diverge. However, it has been found as well that in particular MP2 benefits largely from error cancelation with medium sized basis sets and yields amazingly good results at rather low cost.

3.3 Coupled cluster theory (CC)

Coupled cluster theory comprises the most accurate method to deal with dynamical electron correlation treatment for single-reference states. Whereas perturbation methods include all excitation levels with respect to the reference wavefunction to a given order, CC methods incorporate all excitations up to a given level to infinite order. There is a close connection between CC methods, Møller-Plesset perturbation theory and the configuration interaction method [16]. CC methods are most conveniently expressed in terms of the second-quantization formalism, which goes quite beyond this introductory lecture, so that details are omitted.

In CC theory the wavefunction (intermediate normalization) is expanded exponentially

$$\Psi_{CC} = \exp(\mathcal{T})\Psi_0 = \exp(\mathcal{T})\Phi_0 \quad (22)$$

$$e^{\mathcal{T}} = 1 + \mathcal{T} + 1/2\mathcal{T}^2 + \dots = \sum_{k=0}^{\infty} \frac{\mathcal{T}^k}{k!} \quad (23)$$

$$\mathcal{T} = \sum_i \mathcal{T}_i \quad (24)$$

$$\mathcal{T}_1\Phi_0 = \sum_{ia} t_i^a \tau_i^a \Phi_0 = \sum_{ia} t_i^a \Phi_i^a \quad (25)$$

$$\mathcal{T}_2\Phi_0 = \sum_{ijab} t_{ij}^{ab} \tau_{ij}^{ab} \Phi_0 = \sum_{ijab} t_{ij}^{ab} \Phi_{ij}^{ab} \quad (26)$$

The cluster operators \mathcal{T}_n are linear combinations of excitation operators τ weighted with cluster amplitudes t . Applied to a reference state (here a closed shell Slater determinant) they generate all n th excited Slater determinates with respect to the reference state Ψ_0 . Equation 22 expands thus to

$$\Psi_{CC} = (1 + \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_1^2 + \mathcal{T}_1\mathcal{T}_2 + \mathcal{T}_2^2 + \mathcal{T}_3 \dots)\Psi_0 \quad (27)$$

Inserting 22 into the Schrödinger equation, multiplying from the left with $e^{-\mathcal{T}}$ and projecting against $\{\Phi\}$ such as $\Phi_0, \Phi_i^a \dots$ yields the ground state energy and cluster equations, respectively.

$$\langle \Phi_0 | e^{-\mathcal{T}} (\mathcal{H} - E_0) e^{\mathcal{T}} | \Phi_0 \rangle = \langle \Phi_0 | e^{-\mathcal{T}} \mathcal{H}_N e^{\mathcal{T}} | \Phi_0 \rangle = E_{cc} - E_0 \quad (28)$$

$$\langle \Phi_i^a | e^{-\mathcal{T}} (\mathcal{H}_N + E_0) e^{\mathcal{T}} | \Phi_0 \rangle = 0 \quad (29)$$

E_{cc} solely depends upon singly and doubly excited determinants. However, the equations for the amplitudes form a coupled system of non-linear equations connecting all excitation levels. Still, due to the Hamiltonian containing at most two-electron terms, $e^{-\mathcal{T}} \mathcal{H}_N e^{\mathcal{T}}$ contains at most four-fold products of \mathcal{T} . The equations for the amplitudes are solved iteratively. There is an important distinction between a truncated linear CI expansion and the truncated CC expansion of the wavefunction: since the operator \mathcal{T}_n is implicitly included up to infinite order, up to N -fold excited determinants are included, their coefficients are given by products of the n -fold excitations. This feature makes CC size-extensive, i.e., the energy scales linearly with the number of independent subsystems as required. Truncated CI in contrast recovers zero electron correlation energy per subsystem in the limit of an infinite system size.

Different CC models can be obtained by either limiting the expansion of \mathcal{T} to a maximum excitation level (CCSD: $\mathcal{T} = 1 + \mathcal{T}_1 + \mathcal{T}_2$, CCSDT: $\mathcal{T} = 1 + \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_3$, etc.) and possibly additionally neglecting some terms in the resulting equations (CC2[17], CC3[18]). Since the resulting non-linear equations must be solved iteratively, additional variants are conceivable by sticking to a perturbative solution for a subset of amplitudes (CCSD(T)[16]). As the resulting

amplitude equations for CC methods of high order are nasty – to put it nicely – it is solely by recently developed contraction engines (e.g. [19]), which constitute programs that write optimized (and correct!) code for terms arising in coupled cluster expansions up to arbitrary order getting their input at much higher abstraction level. The computational effort increases with CC2, CCSD, CC3, CCSDT, CCSDTQ as $O(n^5)$, $O(n^6)$, $O(n^7)$, $O(n^8)$, $O(n^{10})$.

Although CC theory is essentially a single-reference treatment, by inclusion of higher excitations it is becoming increasingly robust against multi-reference character, although treatment of bond breaking is out of question. Its prime advantage over CI is its size-extensivity, which makes it the method of choice for electron-rich molecules. Excited states and properties are available through linear response theory [20] connecting the response of the density to time-dependent external fields in order to derive frequency-dependent properties whose poles are located at the excitation energies. An efficient implementation of the CC2 method exploiting the resolution of identity approximation for integral evaluation provides ground and excited state properties including ground state gradients [21]. CC2 is in terms of computational effort and quality of ground state properties similar to MP2 though in contrast to the latter applicable as well to excited states dominated by single excitations with respect to the ground state.

3.4 Multi-reference singly and doubly excited configuration interaction (MR-SDCI)

In the MR-SDCI method the N-electron wavefunction is linearly expanded in terms of the reference configurations and all singly and doubly excited CSFs thereof

$$\Psi_{MRCI} = \sum_i^{ref} c_i^{ref} \Psi_i^{ref} + \sum_{ia} c_i^a \Psi_i^a + \sum_{ij}^{ab} c_{ij}^{ab} \Psi_{ij}^{ab} \quad (30)$$

Continuing this expansion up to N-fold excitations finally yields the FCI expansion. The CIS expansion corresponds to a truncation after single excitations with solely a single reference configuration. Single excitations incorporate the effect of orbital relaxation with respect to the orbital generation step, whereas the double excitations account for the dynamical correlation effect. The energetic contributions decrease in the order D-Q-T-S. Since the Hamilton operator contains at most two-particle terms, all matrix elements between configurations differing by more than double excitations vanish (Slater-Condon-Rules). Variants of this method include MRD-CI [25], treating only a small part of the entire configuration space variationally whereas the remainder is treated as perturbation. Internally contracted MR-SDCI [26] applies single and double excitations to the reference *state* as a single entity only, thereby making the size of the MR-SDCI expansion independent of the size of the reference space. Whereas the unrestricted MR-SDCI method can be applied to any excited state at any nuclear geometry, this does not necessarily apply to all its variants. The lack of size-extensivity can be overcome by using the approximately size-extensive variants MR-AQCC or MR-ACPF [27, 28], which work by renormalization of the wavefunction. Analytical gradients and spin-orbit coupling available as well [29].

3.5 Complete active space perturbation theory to second order (CASPT2)

The CASPT2 method [30] aims at the quantitative description of ground and excited multi-reference states by using single-reference perturbation theory with respect to a multi-reference

zeroth order CASSCF wavefunction. \mathcal{H}_0 is chosen as a generalized Fock operator such that for a closed-shell reference wavefunction the MP2 results are reproduced. Solving for the first-order correction $\Psi_1 = \sum_i c_i \Phi_i$ amounts to solving a linear equation system in the N-electron basis

$$[\mathbf{H}_0 - \tilde{E}_0 \mathbf{I}] \vec{c} = -\vec{v}' \quad \text{with} \quad v_i = \mathbf{H}'_{0i} \quad (31)$$

In contrast to MP2 \mathbf{H}_0 is not diagonal for a general CASSCF wavefunction. Choosing \mathbf{H}_0 as to decouple the triply and higher excited determinants from the remainder ensures that the first-order correction of the wavefunction can be solely expanded within all singly and doubly excited determinants. As any element of \mathbf{H}_0 can be written as a linear combination of elements of an effective (orbital) Fock matrix \mathbf{f} , further simplifications arise by transforming the orbital basis such as to minimize the off-diagonal elements of \mathbf{f} . Yet, the left hand side matrix of eqn. 31 contains many off-diagonal elements and requires – in contrast to MP2 – an iterative solution, which might be difficult to converge.

This approach has been very successfully applied to ground and excited states [31]. A weak point is the sensitivity to so-called intruder states, i.e., matrix elements with respect to \mathcal{H}_0 of configurations outside the CASSCF space that lie energetically rather close to those included in the variational CASSCF treatment cause the energy expression to diverge similar to MP2 (eqn. 21). This situation has much improved upon the introduction of imaginary level shift [32]. However, if intruder states arise from strong coupling with the exact Hamiltonian, there is no way but to enlarge the CASSCF space. As Møller-Plesset perturbation theory, the CASPTn series potentially diverges. Regions close to avoided crossings must be treated by the multi-state variant [33].

3.6 Møller-Plesset perturbation theory with explicit r_{12} terms (MP-R12)

Owing to the mathematical form of the Hamiltonian containing the singular term $\frac{1}{|r_1 - r_2|} = \frac{1}{r_{12}}$ the wavefunction must behave close to the interelectronic coalescence point as

$$\left. \frac{\partial \Psi(r_{12})}{\partial r_{12}} \right|_{r_{12}=0} = \frac{1}{2} \Psi(r_{12} = 0) \quad (32)$$

implying that the unnormalized wavefunction contains terms *linear* in the interelectronic distance (Kato's cusp condition [13]). However, products of one-electron basis functions (GTOs) contain no terms of odd order in r_{12} , thereby being responsible for the slow convergence with respect to basis set size. This *angular* correlation depends on the angular momentum l of the basis functions. For He it has been found that the correlation energy error δE_{corr} behaves as

$$\delta E_{corr} \approx \frac{1}{(l+1)^3} \quad (33)$$

Introducing terms linear in r_{12} therefore aims at improving basis set convergence and in the limit of a complete basis set r_{12} variants of quantum chemical methods should give the same results as their conventional counterparts. Using the ansatz [34, 35]

$$\Psi^{(1)} = \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{ij} d_{ij} \tilde{\Phi}_{ij} \quad (34)$$

for the first-order wavefunction. $\tilde{\Phi}_{ij}$ denotes linear combinations of products in r_{ij} times the HF wavefunction appropriately antisymmetrized and orthogonal to all $\{\Phi_0, \Phi_{ij}^{ab}\}$. Evaluating the

second-order energy by minimizing the Hylleraas functional requires the evaluation of three- and four-electron integrals which are not only difficult to evaluate but also numerous (up to $O(n^8)$). Introducing approximations based upon the resolution of identity allows to get rid of the most difficult and numerous three- and four-electron integrals. The approximations are chosen such as to become exact in the limit of a complete basis and to guarantee that the basis set limit is reached much faster than in conventional calculations. Still, reliable results require somewhat larger basis sets with high-angular momentum functions (including up to at least f type functions) thereby limiting the range of applicability of this method. This approach has also extended to the more complex Coupled Cluster [36] method. The excellent results of MP-R12, which converges as $(l+1)^{-7}$ to the basis set limit, are frequently used as benchmark data for basis set convergence studies (e.g. [37]). Recent work is directed to removing the restriction to large basis sets by introducing an auxiliary basis set to evaluate the intermediate terms so that the resolution of identity approximation holds independently of the size of the actual basis set used.

3.7 Local Møller-Plesset perturbation theory (LMP2)

Local electron correlation methods aim at linear scaling with the size of the molecule. Conventional implementations scale unfavourably as $\geq O(n^5)$. The basic idea is to exploit the short-range character of dynamic electron correlation. Conventional single-reference electron correlation methods expand the configuration space in terms of the canonical and mostly delocalized HF orbitals obviating this aim. However, the HF wavefunction does not change upon unitary transformation of the MOs mixing solely occupied and unoccupied orbitals separately. Thus, the LMP2 method [38] localizes the occupied orbitals (LMOs) and spans the orthogonal complement by non-orthogonal projected atom centered basis functions (PAOs). From orbital domains, comprised of those PAOs *spatially* close to a given LMO, pair domains composed of products of two orbital domains are constructed. The size of an orbital domain is independent of the molecular size. In addition, by grouping $O(n^2)$ pair domains into different classes depending upon the spatial distance of the respective orbital domains, the number of pairs which significantly contribute to the energy scales only linearly with system size. Again, like CASPT2, due to the orbital basis \mathbf{H}_0 is not diagonal and an iterative procedure based on optimizing the Hylleraas functional is used to obtain Ψ_1 . The number of terms Ψ_1 is expanded into scales only linearly with system size. The evaluation of the matrix elements of \mathbf{H}_0 and \mathbf{H}' can be substantially sped up by local density fitting [39]. Density-Fitting LMP2 calculations are reported for medium sized systems to be faster than the corresponding HF calculation.

4 Conclusions

For states qualitatively well-described by the HF method, there are several different methods available to incorporate electron correlation. Whereas CCSDT is rather robust and accurate albeit applicable to small systems, only, the cheaper CC2 and CCSD methods are also applicable to excited states (dominated by single excitations) and far less limited in system size. MP2 is restricted to ground states and more prone to failure although it seems to largely benefit from error cancelation. MP2-R12 is the method of choice to go for the one-electron basis set limit. Local MP2 on the other hand, seems to be ultimately promising for dealing with large systems – the main difficulty here is to construct the HF wavefunction which is going to be (much) more

expensive than the electron correlation treatment.

For multi-configurational states there are few methods available notably perturbation theory CASPT2 and MR-SDCI/MRAQCC. Whereas the latter is completely generally applicable the perturbational approach faces problems close to avoided crossings and might suffer from intruder states. CASPT2 is primarily limited by the size of the CAS but otherwise widely applicable to ground and excited states. MRSDCI/MRAQCC is confronted by the polynomial growth of the configuration space which reaches easily 10^9 configurations even for small molecules.

Further reading

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