Basis Sets, Accuracy,
and Calibration in Quantum Chemistry

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This lecture primarily deals with aspects of quantum chemical *ab initio* cluster codes without periodic boundary conditions. The most important parameters, which any user of quantum chemical program packages must select when setting up a problem is the choice of the model Hamiltonian and the one-electron and N-electron basis set. As there is no general fool-proof recipe available that covers the general case, we approach the problem by discussing the most relevant approximations and their implications. The aim is to provide the reader with a basic idea of the various approximations and to what extent results and conclusions maybe affected. Finally it is anticipated that most readers will not carry out quantum chemical calculations for their own sake but rather use them as a tool to extract data to be processed further for the investigation of the problem in question. Here, selecting an appropriate theoretical method and being aware of their potential shortcomings is even more important as not to jump to entirely false conclusions. Following a short review of the basic models and approximations, the major errors are discussed in some detail. Extrapolation and calibration methods are presented and illustrative case studies are discussed.

1 Introduction

Although the general aim is to strive for (highly) accurate solutions of the many-body Schrödinger equation this is possible only for the smallest systems because the resource requirements in terms of computer time, memory and disk space increase rather unfavourably with the size of the system. However, in many cases there is no need to carry out calculations at high accuracy since experimental problems associated with larger systems limit the resolution and correspondingly theoretical treatment of lower accuracy may be perfectly sufficient. Frequently, even semiquantitative answers are all that is needed and occasionally apparently simple problems are hard to solve accurate enough. Thus the notion of accuracy depends upon the specific problem in question.

A central aspect of quantum chemistry is the explicit or implicit determination of state-specific potential energy surfaces (PES), predicting geometries, spectra and chemical reactions. As these properties solely depend upon *relative* energies accurate calculations need to reproduce the shape of the exact PES. In fact most quantum chemical models are not generally applicable to arbitrary sections of the PES. Properties, which primarily sample regions of the electron density of little importance for the energy require some care. The requirements for their calculation may be drastically different from those for the energy. Hyperpolarizabilities, which determine various nonlinear optical effects, for example depend on the outer charge density distribution and are quite sensitive to dynamic electron correlation effects.

Being aware about the conceptual limitations of methods and to anticipate the applicability of a given approach is essential. It is advisable to judge the accuracy of quantum chemical calculations not simply by comparison to experiment. Experimental data frequently cannot be compared to quantum chemical results without further corrections for effects not included in the (quantum chemical) model Hamiltonian and the processing of the experimental raw data itself relies frequently on assumptions, which may or may not hold accurately enough. This might render an interpretation of the deviation impossible. It is quite tempting to adjust the various parameters of a quantum chemical calculation such that the results finally agree with the available experimental data one has set out to reproduce or to explain. This is - apart from possibly leading to entirely wrong conclusions - entirely useless, since it prevents us from analysing the result and thereby attaining a better understanding of the underlying problem beyond merely generating a collection of numbers.

The preferred approach is to assess the quality of a calculation within the theoretical approach. Comparison with experimental data follows as the second step. Constructing series of calculations in order to detect or to eliminate possible sources of error as well as using series of calculations of increasing accuracy for suitably chosen reference systems to calibrate the methods whenever necessary. Finally, extrapolation techniques may prove helpful in order to overcome practical limitations associated with the wave function expansion.

2 Basic Approximations

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

$$\mathcal{H} = -\tfrac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iA} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{A>B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \qquad (1)$$

$$= -\tfrac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} r_{ij}^{-1} - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} \qquad (2)$$

$$= \mathcal{T}_e + \mathcal{V}_{ee} + \mathcal{V}_{ne} + V_{nn}. \qquad (3)$$

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. The impact of spin-orbit coupling may be of similar importance as electron correlation for the heavier elements and cannot be straightforwardly ignored (cf. Section 3.6).

The Born-Oppenheimer approximation[1,2], sometimes referred to as *adiabatic* approximation[3], decouples electron motion from the motion of the nuclei. It works well wherever the gradient of the electronic wave function 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[4].

2.2 Wave Function Expansion

The eigenvalues and eigenfunctions of the time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{4}$$

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 wave function $\hat{\Psi}(\alpha)$, which depends on a set of parameters $\{\alpha\}$ the energy functional runs

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

By virtue of the variation theorem the approximation $\hat{E}(\alpha)$ is an upper bound to the exact energy of Eq. (4) and the wave function $\hat{\Psi}(\alpha)$ will converge on average to the exact wave function Ψ. Using a linear expansion in α and making the energy stationary

$$\hat{\Psi}(\alpha) = \sum_i \alpha_i \Phi_i \tag{6}$$

with respect to α yields a generalized eigenvalue problem

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \tag{7}$$

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

$$\mathbf{S}_{ij} = \langle \Phi_i|\Phi_j\rangle \tag{9}$$

$\mathbf{H}_{ij}$ and $\mathbf{S}_{ij}$ denote the hamiltonian and overlap matrix elements with respect to the N-particle 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 basis may be chosen orthonormal, the overlap matrix is replaced by the unit matrix. A complete N-particle basis set yields the exact solution of Eq. (4). However, such a basis would be infinite in size and rather impractical to use.

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 Eq. (8). Conventionally, the N-electron basis is constructed from antisymmetrized products of orthonormal spinorbitals $\phi_{ki}(\mathbf{r}_i)$, denoted Slater determinants Φ.

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

The spinorbitals are a product of a spatial part $\tilde{\phi}_{ki}(\mathbf{r}_i)$ times a spin part $\sigma_i(\omega_i)$. The spatial part is expanded in linear combinations of atom-centered one-electron basis functions χ_μ. The favourable mathematical properties of Gaussian Type Orbitals (GTOs) for integral evaluation make them the preferred choice for $\chi_\mu(\mathbf{r})$.

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

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

The major challenge is the evaluation of the two-electron integrals over GTOs (Eq. (13)) that finally occur as the basic building blocks of the matrix elements $\langle \Phi_i | \mathcal{H} | \Phi_j \rangle$. $(..|..)$ and $[..|..]$ indicate integrals over spatial orbitals and spinorbitals, respectively.

$$(\mu\nu|\kappa\lambda) = \int \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_\kappa(\mathbf{r}_2)\chi_\lambda(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{13}$$

$$(ij|kl) = \int \tilde{\phi}_i(\mathbf{r}_1)\tilde{\phi}_j(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tilde{\phi}_k(\mathbf{r}_2)\tilde{\phi}_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{14}$$

$$[ij|kl] = \int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2) d\tau_1 d\tau_2 \tag{15}$$

$$[ij|kl] = \langle ik|jl \rangle \qquad \langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle \tag{16}$$

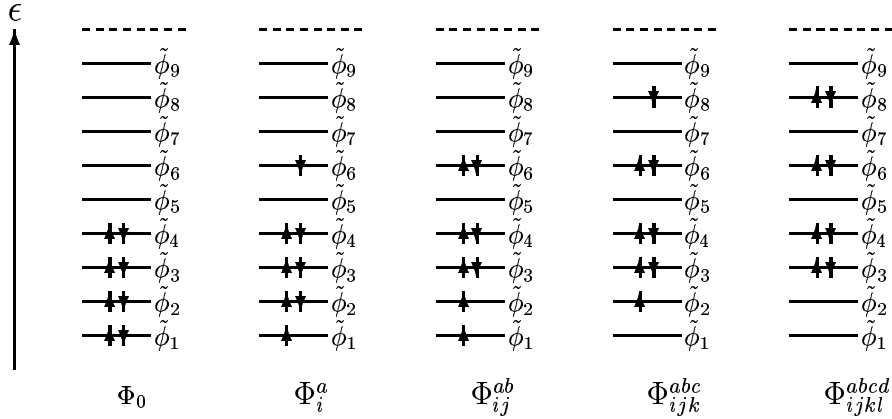$$(ij|kl) = (ji|kl) = (ij|lk) = (ji|lk) = (kl|ij) = (lk|ij) = (kl|ji) = (lk|ji) \tag{17}$$

Figure 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.

Figure 1 schematically depicts the construction of the N-particle basis set. The molecular orbital (MO) coefficients $C_{\mu i}$ are usually obtained from Hartree-Fock (HF) or multi-configurational self-consistent field (MCSCF) calculations. Whereas in the HF method $\hat{\Psi}(\alpha)$ is expanded in a single Slater determinant the MCSCF method expands $\hat{\Psi}(\alpha)$ into a small expansion of usually less than 50000 terms (cf. Eq. (6)). In either case *all* parameters

$\{\alpha\}$ and $C_{\mu i}$ are fully optimized. The MOs $\tilde{\phi}_i$ are ordered according to their eigenvalues (orbital energies ϵ_i). The ground (or reference) state is constructed by filling the energetically lowest-lying orbitals with two electrons each (closed shell case). Singly, doubly, triply and quadruply excited determinants are obtained by "exciting" electrons from some occupied to unoccupied orbitals. Continuing up to N-fold excitations generates the full N-particle basis. Slater determinants are in general no eigenfunctions to $\mathcal{S}^2$. However, spin-adapted configurations (CSFs) may be constructed by taking the appropriate linear combinations of Slater determinants.

The number of CSFs that can be constructed from n molecular orbitals and N electrons subject to a spin-multiplicity of $S = b/2$ is given by[5]:

$$N_{csf} = \frac{b+1}{n+1} \binom{n+1}{a} \binom{n+1}{n-a-b} \quad \text{where } N = 2a + b \;\; S = b/2 \qquad (18)$$

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 basis sets used in HF calculations whereas $n = 2N$ is about the minimum size for basis sets suitable for electron correlation methods. Evidently, using the linear expansion of the wave function (Eq. (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. FCI calculations can be carried out for expansion lengths beyond 1 billion terms[6]. *The truncation of the one- and N-particle basis are the most important errors in quantum chemical calculations.*

2.3 Non-Dynamical Versus Dynamical Electron Correlation

Truncating the N-electron basis to a single determinant and variational optimization of the MO coefficients defines the HF method. Since the canonical HF orbitals form the basis for most advanced electron correlation methods, the electron correlation energy is defined as the difference between the exact non-relativistic energy at 0 K and its HF counterpart in a *complete* basis $\{\Phi\}$:

$$E_{corr} = E_{exact} - E_{HF,\infty} \qquad (19)$$

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

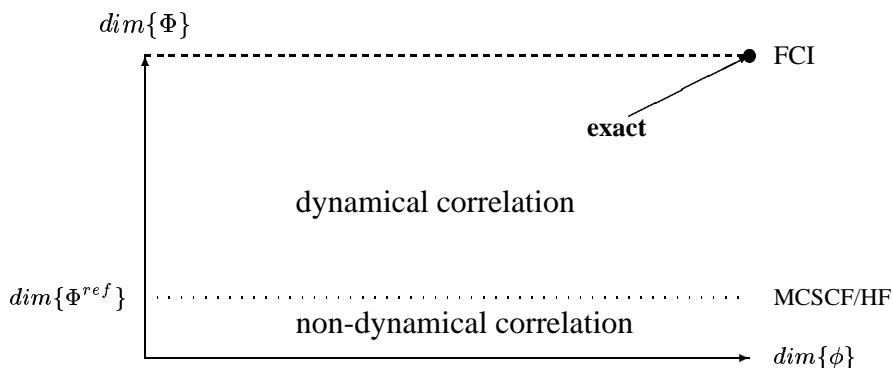|	n=N	n=2N
N	N_{csf}	N_{csf}
4	20	336
8	1 764	866 320
12	226 512	3 405 278 800
16	34 763 300	16 226 413 117 200
20	5 924 217 936	86 391 974 193 251 584
24	1 081 724 803 600	494 452 245 428 329 102 096

Figure 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.

E_{exact} is apart from one- and two-electron systems unknown and must be obtained from experimental data corrected for relativistic effects. In some cases Quantum Monte Carlo techniques may provide accurate reference data. Considering electron correlation as the inadequacy of expanding the N-electron wave function in a single Slater determinant (or a single CSF) two different effects can be identified.

The HF wave function by itself may be even qualitatively incorrect due to near-degeneracy effects: low-lying configurations strongly interact with each other resulting in large off-diagonal elements of **H** (Eq. (7)), so that the wave function 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 disrupture or bond breaking. Computing chemical reaction paths accurately requires the balanced (or unbiased) description of all intermediate structures so that the minimum configuration space is the joined set of all near-degenerate configurations along the path. Treating several electronic states on the same footing requires similar measures to ensure unbiased treatment.

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 Katos cusp condition[7]: there is a singularity in the Hamiltonian close to the coalescence point, where the interelectronic distance of a pair of electrons $r_{ij} \rightarrow 0$ 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 wave function.

Electron correlation methods aim at approximating the FCI result, i.e. expanding the wave function 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 (cf. Figure 2).

2.4 One-Electron Basis Sets

For the ground state of Helium it has been empirically found that the energy contribution of an individual orbital with quantum numbers nml solely depends upon the principal quantum number. This finding suggests the construction of basis set hierarchies such that the next level of accuracy should include all orbitals of the corresponding principal quantum number. Thus, the minimum basis set e.g. for carbon amounts to the n=1,2 (2s1p). Incremented by one set of polarization functions n=3 (1s1p1d) gives the double zeta (DZ), adding another set n=4 (1s1p1d1f) yields the triple zeta (TZ) basis etc. These atomic basis functions are built from contracted GTOs (CGTOs) i.e. fixed linear combinations of primitive GTOs. So far only the number and angular momentum CGTOs is fixed. Contraction length, contraction coefficients and exponents of the individual primitive GTOs are determined by minimizing the averaged energy over one or several atomic states at HF (for minimum basis sets) and correlated level. Further optimization might also involve diatomics especially of the heavier elements in order to improve the applicability to molecular calculations. The exponents of the primitive GTOs are often chosen to (partially) form an even-tempered series, i.e. $\alpha_i = \alpha_{i-1}\beta$.
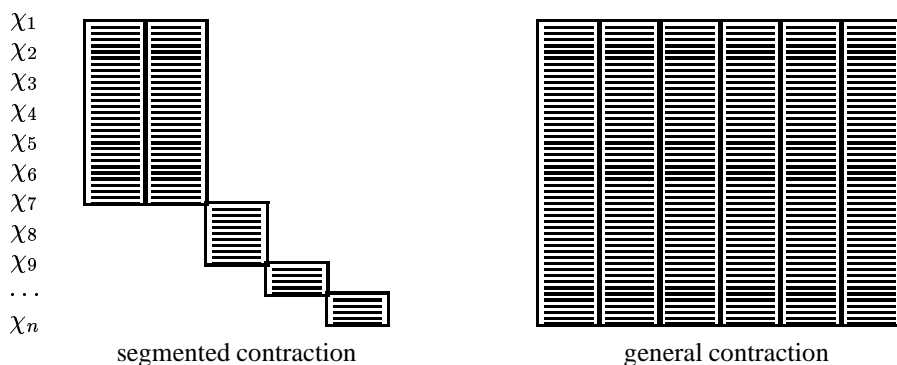

Figure 3. Segmented vs. generally contracted basis sets. All primitive GTOs χ_μ belong to the same angular momentum quantum number $l = m_\mu + l_\mu + n_n u$.

There are two types of basis sets denoted generally contracted and segmented. Whereas segmented basis sets aim at minimizing the contraction length and thus the number of primitive integrals to evaluate, the general contractions exploit reusing intermediate quantities for an entire contraction set at the expense of large contraction lengths. Most integral codes favour one or the other basis set type.

Initially, the concept to add all basis functions belonging to a given principle number simultaneously was taken advantage of by the atomic-natural orbital (ANO) basis sets[8] They form generally contracted basis sets and the contraction coefficients are obtained as the eigenvectors of the one-electron density matrix with the largest eigenvalues (occupation

numbers). Thus given the number of primitives and their exponents the density matrix averaged over several low-lying atomic states based on some electron correlation method in the primitive GTO basis is computed. The NOs with the highest occupation numbers are used to define the contraction coefficients of the basis set. The ANO basis sets are now available for almost the entire periodic table[10,9,11].

The segmented *correlation consistent basis sets* (cc-pVXZ,cc-pCVXZ, aug-cc-pVXZ, X=D,T,Q,5,6) by Dunning and co-workers[12,13]. They have been shown to form a balanced sequence of increasing accuracy and have been often used for extrapolation of properties to the complete basis set (CBS) limit. Finally, there are segmented basis sets introduced by Ahlrichs and co-workers[14,15], whose main emphasis was to provide compact basis sets well-suited for correlated molecular calculations. Many basis sets are available from `http://www.emsl.pnl.gov/forms/basisform.html`.

Obviously, the choice of the one-electron basis is crucial for the quality of a calculation. Turning primarily to "simple properties" such as geometries and vibrational frequencies, their calculation at the uncorrelated (HF) level of theory can be carried out reasonably accurate (vibrational frequencies with empirical scaling only) with DZ quality basis sets. Using electron correlation methods (including DFT!) requires usually at least TZ quality basis sets. Turning to properties, which sample the electron density distribution in regions spatially different from those relevant for the energy gives rise to more stringent basis set requirements. Static electric multipole moments, sample $\langle r^n \rangle$ so that not only very diffuse basis functions but also those of *higher angular momentum* are required. In addition the result is sensitive to the level of dynamic electron correlation treatment. To describe Rydberg states also calls for very diffuse basis functions, even to obtain qualitatively correct results. Similarly, there is no point in correlating the non-valence electrons of a molecule while using a standard polarized valence basis set, as they are insufficiently flexible to incorporate core and core-valence correlation at all. However, the core-electrons contribute substantially to the correlation energy as they are spatially close to each other, thereby forcing energetically favourable but (with inadequate basis sets) artificial valence electron density distributions. In summary, correlating core electrons without basis sets augmented by tight basis functions including those of high angular momentum, at best is a waste of computer time and at worst deteriorates the quality of the calculation.

2.5 Electron Correlation Methods: N-Electron Basis Truncation

Electron correlation methods aim at approximating the exact solution within a given one-electron basis set by truncating the full N-electron basis in some systematic way. Basically three different methods with many individual variants are in use: configuration interaction, perturbation theory and coupled-cluster methods.

The multi-reference configuration interaction (MRCI) method expands the wave function linearly in the N-electron basis. Truncation is achieved by defining a reference space and restricting the configuration space to single and double excitations out of each configuration contained in the reference space, which is chosen such as to deal with the non-dynamical electron correlation.

$$\Psi_{MRCI} = \sum_i^{ref} c_i^{ref} \Psi_i^{ref} + \sum_{ia} c_i^a \Psi_i^a + \sum_{ij}^{ab} \Psi_{ij}^{ab} \tag{20}$$

There are several variants of this method. Internally contracted MRCI[16] restricts the reference space to a single multi-configurational wave function thereby making the size of the configuration space independent of the size of the reference configuration space. Other variants treat only a part of the configuration space variationally while the remaining configurations enter through perturbation theory[17].

Perturbation theory splits the Hamilton operator into a zeroth order approximation and a fluctuation potential. Non-degenerate (or single-reference) Møller-Plesset (MP) perturbation theory uses the Fock operator as zeroth order approximation, thus all eigenvalues and eigenvectors are available straight from the initial HF calculation. Working in the canonical HF orbital basis, energies up to third order are available straight away. The notation $\langle 0|\mathcal{O}|n\rangle$ denotes the matrix element between the ground state determinant and any excited determinant (solutions of $\mathcal{F}$, eigenvalues E_i, orbital energies ϵ_i).

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' = \mathcal{F} + \mathcal{H}' \tag{21}$$

$$E = E_0 + \sum_{i=1}^{\infty} \tilde{E}_i \tag{22}$$

$$E_0 = \langle 0|\mathcal{H}_0|0\rangle = \sum_i 2\epsilon_i \tag{23}$$

$$\tilde{E}_1 = \langle i|\mathcal{H}'|i\rangle = E^{HF} - E_0 \tag{24}$$

$$\tilde{E}_2 = \sum_{n\neq 0} \frac{|\langle 0|\mathcal{H}'|n\rangle|^2}{E_0 - E_n} = \sum_{\substack{i<j \\ a<b}} \frac{|\langle \Phi_{ij}^{ab}|\mathcal{H}'|\Phi_0\rangle|^2}{\langle \Phi_{ij}^{ab}|\mathcal{H}_0 - E_0|\Phi_{ij}^{ab}\rangle} = \sum_{\substack{i<j \\ a<v}} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{25}$$

$$\tilde{E}_3 = \sum_{nm\neq 0} \frac{\langle 0|\mathcal{H}'|n\rangle\langle n|\mathcal{H}'|m\rangle\langle m|\mathcal{H}'|0\rangle}{(E_0 - E_n)(E_0 - E_m)} - E_{HF} \sum_{n\neq 0} \frac{|\langle 0|\mathcal{H}'|n\rangle|^2}{(E_0 - E_n)^2} \tag{26}$$

Important variants thereof include CASPT2[18] using a single-reference multi-configurational zeroth order wave function, which has been successfully applied to a wide variety of ground and excited states[19].

coupled-cluster (CC) methods invoke a non-linear expansion of the wave function.

$$\Psi_{CC} = e^{\mathcal{T}}\Psi_0 = e^{\mathcal{T}}\Phi_0 \tag{27}$$

$$e^{\mathcal{T}} = 1 + \mathcal{T} + \frac{1}{2}\mathcal{T}^2 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!}\mathcal{T}^k \tag{28}$$

$$\mathcal{T} = \sum_i \mathcal{T}_i \tag{29}$$

$$\mathcal{T}_1\Phi_0 = \sum_{ia} t_i^a \tau_i^a \Phi_0 = \sum_{ia} t_i^a \Phi_i^a \tag{30}$$

$$\mathcal{T}_2\Phi_0 = \sum_{ijab} t_{ij}^{ab} \tau_{ij}^{ab} \Phi_0 = \sum_{ijab} t_{ij}^{ab} \Phi_{ij}^{ab} \tag{31}$$

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 nth excited Slater determinantes with respect to the reference state Ψ_0. Eq. (27) expands thus to

$$\Psi_{CC} = (1 + \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_1^2 + \mathcal{T}_1\mathcal{T}_2 + \mathcal{T}_2^2 + \mathcal{T}_3 + \ldots)\Psi_0 \tag{32}$$

All these wave function based expansions - in principle - can be improved systematically in order to approach the FCI limit: MRCI may either increase the excitation level or enlarge the reference space. Perturbation theory can be continued up to high order and in the coupled-cluster method the cluster operator (Eq. (29)) maybe truncated at N^{th} excitation level. As the MPn series may diverge, the coupled-cluster method is more expensive but more reliable. A serious drawback of MPn and CC approaches is the limitation to single reference cases.

Density functional theory is somewhat special as electron correlation and exchange are treated through a more or less well-founded correlation-exchange functional of the one-electron density. There is no direct way connecting wave function expansions with DFT. Owing to the limited knowledge about the properties of the *exact* exchange-correlation functional, there can be done little about *systematic* improving DFT towards the FCI limit. In terms of computational efficiency DFT is by far superior to Hartree-Fock and electron correlation methods (maybe with exception of *local* MP2[20]). Compared to electron correlation methods, DFT results display a considerable spread in accuracy depending upon the specific case as well as the utilized functional whereas they are almost always superior to HF.

3 Errors

3.1 Basis Set Truncation Errors

To this end we can define the apparent error as the difference between the true solution of the electronic Schrödinger equation (corresponding to the experimental value corrected for non-BO effects and possibly relativistic corrections). This can further be subdivided into the basis set error associated with the limited size of the 1-electron particle basis and the n-electron error associated with the incompleteness of the n-electron basis. In the limit of a complete basis set the basis set error vanishes and solely the n-electron error remains denoted the *intrinsic error* of the corresponding model.

One-electron basis set truncation errors may be very large, especially if basis sets entirely inadequate to the given problem or the desired accuracy are chosen. Under the assumption, that non-dynamical electron correlation plays no role, good theoretical estimates

method	pCVDZ $[10s2p2d]$	pCVTZ	pCVQZ	pCV5Z	pCV6Z	56-expln.
MP2	-382.7	-477.8	-510.7	-523.1	-528.7	-536.4
CCSD	-387.8	-478.2	-507.1	-516.7	-520.6	-525.9
CCSD(T)	-400.4	-498.0	-528.5	-538.7	-542.7	-548.3

Table 2. Recovered electron correlation in mE_h for N_2 at equilibrium distance $R_{N-N} = 109.77pm$. Estimated basis set limits: -537.2 (MP-R12), -526.2 (CCSD-R12), -548.2 (CCSD(T)-R12). Taken from Ref. 23. All electrons correlated. 56-expln=(216 E(pCV6Z)-125 E(pCV5Z))/91.

method	pVDZ	pVTZ	pVQZ	pV5Z	45 expln.	est. intr. error
MP2	213.36	229.23	235.78	238.36	241.1	+12.7
MP3	191.31	205.76	212.14	214.31	216.6	-11.8
MP4	203.58	221.13	227.98	230.41	232.9	+4.5
CCSD	193.67	207.98	214.17	216.28	218.5	-9.9
CCSD(T)	200.69	216.70	223.17	225.42	227.8	-0.6
IMRCI	201.96	217.90	224.19	226.31	228.5	+0.1
IMRCI+Q	200.74	216.62	223.14	225.37	227.7	-0.7

Table 3. Computed Dissociation energy in kcal/mol for N_2.
Experiment: 228.4 kcal/mol. 45-extrapolation=$\frac{125 D_e (pV5Z) - 64 D_e (pVQZ)}{61}$. Except extrapolation taken from Ref. 24. Estimated intrinsic error taken as the difference between experimental value and 45-extrapolation.

of the CBS limit can be obtained from the so-called R12-methods, which expand the wave functions explicitly including terms linear in R12. This allows for a more accurate description of the electron-electron cusp (Katos cusp condition). In particular the relatively cheap MP-R12 method[21, 22] has been frequently used for benchmarking the CBS limit. Table 2 demonstrates that only by employing very large basis sets up to including i functions for the nitrogen molecule it is possible to recover more than 98% of the correlation energy. Hence, only extrapolation to the basis set limit (cf. Section 4.1) is a practical way to (almost) quantitatively take care of electron correlation. The differences in the estimated basis set limits indicate that the impact of N-electron basis set truncation is of the order of $10 \, mE_h$.

Systematic expansion of the N-electron basis towards the FCI limit is in principle possible by the MPn perturbation series or by coupled-cluster methods truncating the cluster operator at higher and higher excitations. From the practical point of view either approach is limited to rather small basis sets and small systems. Fortunately, energy *differences* converge more rapidly. In fact, IMRCI+Q/IMRCI and CCSD(T) are almost equivalent whereas CCSD is clearly insufficient and MPn displays an oscillating behaviour going from low to higher order. Note, that even at the cc-pV5Z level the one-electron basis set error is about 2-3 kcal/mol.

3.2 Basis Set Superposition Error

The basis set superposition error (BSSE) is a spurious contribution to the interaction energy arising form the improved description of each fragment in the total basis as compared to the fragment basis alone. It is ultimately a consequence of the one-electron basis set incompleteness. Evidently, the BSSE error will vanish asymptotically as the complete one-electron basis is approached. BSSE appears whenever the molecular geometry is changed and is particularly important for the computation of interaction energies. Without correction an artificial increased binding energy is obtained. In particular when using modest basis sets, BSSE can result in substantial distortions of the PES.

A conceptually simple method to account for BSSE is the counterpoise correction method[25] in which the energies of the fragments are computed in the full basis of the entire complex and subtracted from the energy of the entire system. Although there is some debate about its accuracy it is the procedure of choice to account for BSSE (cf. a
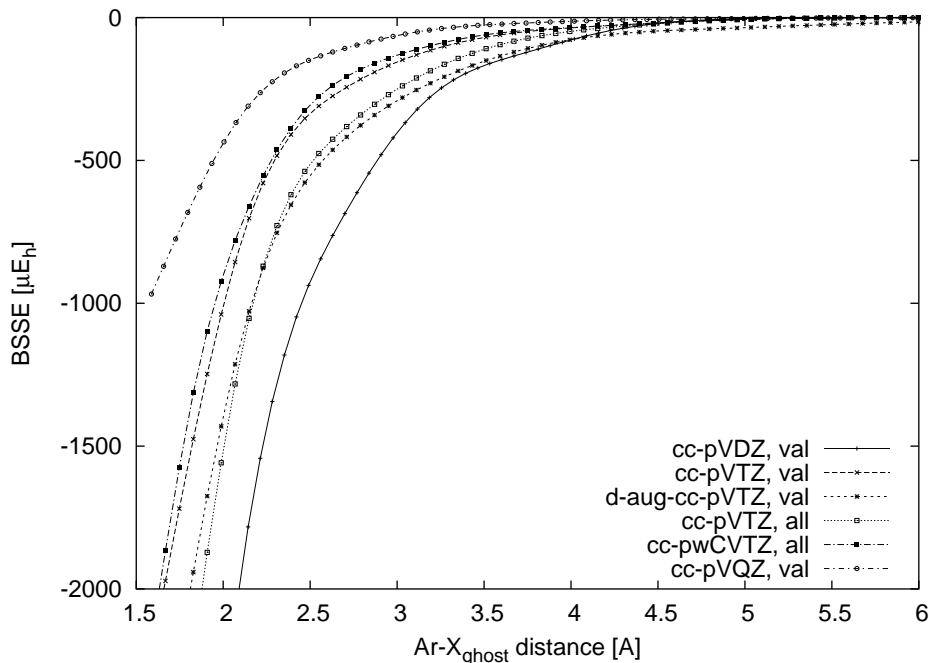
Figure 4. Basis set superposition error for Ar augmented by an Ar ghost basis centered at distance d computed at the CISD level of theory. Van der Waals radius of Ar is 1.88 Å, empirical well depth for Ar_2 is estimated to 99.7 cm^{-1} (453.6μE_h) at d=3.757Å.

review on counterpoise theory[26]).

Investigations on N_2 indicate a BSSE error at experimental equilibrium distance of about 0.8 kcal/mol for TZ and about 0.4 kcal/mol for QZ basis sets. Accurate extrapolation to the complete basis set limit therefore must correct for BSSE prior to extrapolation. BSSE, however, also can be viewed as a basis set incompleteness indicator and thus used to correct the binding energy by adding an *empirical* fraction of the BSSE to correct for basis set incompleteness.

Figure 4 illustrates the BSSE error for Ar in presence of an Ar ghost basis using a variety of Dunnings correlation consistent basis sets at the CISD level of theory. BSSE is moderately method dependent but the trends discussed here hold in general. Increasing the cardinal number of a given basis reduces the BSSE error substantially. Valence electron correlation basis sets and core valence basis sets show a similar BSSE error. Adding diffuse functions strongly increases the BSSE and it vanishes much more slowly with increasing distance to the ghost basis. As a note of caution, correlating the core electrons in a valence basis almost doubles the BSSE error (without improving the results). Although the BSSE error is somewhat method-dependent the conclusions are generally applicable.

The argon dimer forms a van-der-Waals complex kept stable solely by dispersion, which is solely an dynamic electron correlation effect. To properly describe such kind of complexes several sets of diffuse functions are required. At the experimental equilibrium distance of Ar_2 the BSSE correction (twice the Ar-X interaction energy) amounts to

about $250\mu E_h$, i.e. about 50% overbinding for Ar_2 due to BSSE. As increasing the level of electron correlation treatment increases the well depth while increasing the basis set size on the one hand side improves the description of electron correlation effects and on the other hand side decreases the well depth due to reduced BSSE error, one can easily be trapped by error compensation effects. An MP2 calculation with the aug-cc-pVTZ basis accidentally agrees quite well with the experimental well depth.

3.3 Core-Core and Core-Valence Electron Correlation

Core-core (CC) correlation are denoted electron correlation effects solely restricted to the core electrons while core-valence (CV) correlation describes the relaxation of the core electrons upon valence electron correlation and vice versa. Although core and core-valence electron correlation in absolute terms contributes largely to the total correlation energy (N_2: $E_{corr}^{val} = 408mE_h$, $E_{core}^{all} = 548mE_h$[23]), its differential effects on the electron distribution of the valence shells are modest. For compounds of first and second row elements the effects are fairly small. The dissociation energy of N_2 e.g. changes by about 1.5 kcal/mol[27], and the depth of the van-der-Waals minimum for Ar_2 is affected by about $4\mu E_h$[28] corresponding to about 1% of the valence electron correlation contribution. Hence, for the light atoms CC and CV correlation effects need to be considered for high-accuracy calculations, only.

Note, that accounting for CC and CV correlation requires large basis sets and the treatment of many electrons rendering calculations demanding. However, even though solely correlating the valence electrons, the basis set must contain all AOs representing the inner-shell electrons. This sparked the idea of representing the inner-shell electrons by a suitably parametrized potential as to reduce the basis set size denoted effective core potential (ECPs) in contrast to all-electron methods. ECPs are applicable if the relaxation of the core electrons upon chemical binding or valence electron correlation can be neglected. Of course ECPs of neighbouring atoms must not overlap.

There are two different classes of ECPs: the pseudo orbital type[29,30], which replaces the valence orbitals by nodeless pseudo-potentials resembling the HF valence orbitals as much as possible (in the sense of shape and orbital energies) and the core electrons by a potential (containing angular momentum projection operators $\mathcal{P}_l = |l\rangle\langle l|$) of the form

$$U(r) = U_L(r) + \sum_{l=0}^{L-1} U_l(r)\mathcal{P}_l \tag{33}$$

where $L - 1$ is the maximum angular momentum of the core electrons. The potentials $U_l(r)$ and pseudo orbitals are fitted to an analytic form involving Gaussians. The ab initio

model potentials (AIMP) method[31, 32] uses valence orbitals of the correct nodal structure.

$$\mathcal{H} = \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_A -\tfrac{Z_{eff}^A}{r_{iAi}} + V_{coul}^A(i) + V_{exch}^A(i) + P^A + \sum_{i>j} r_{ij}^{-1} + V_{nn} \quad (34)$$

$$V_{coul}^A(i) = -\frac{Z_{core}^A}{r_{Ai}} + 2\sum_c^{core(A)} J_c(i) \approx \sum_k A_k r_i^{n_k} exp(-\alpha_k r_i^2)/r_i \quad (35)$$

$$V_{exch}^A(i) = -\sum_c^{core(A)} K_c(i) = \text{non-local representation} \quad (36)$$

$$P^A = \sum_c^{core(A)} 2\epsilon_c |\Phi_c\rangle\langle\Phi_c| \quad (37)$$

Partitioning the orbital space into core and valence orbitals the effective core potential is derived by a local representation of the Coulomb potential and a spectral representation of the exchange potential, i.e. the core electrons are replaced by the HF potential. In order to ensure the orthogonality of core and valence orbitals and to avoid collapsing the valence orbitals into the core space, a level shifter is added shifting the core orbitals to positive energies, so that they give a positive contribution to the valence orbital energy unless the valence orbitals are orthogonal to the core orbitals. The specification of AIMPs involves apart from the local and non-local potential expansions a basis set expansion of the core orbitals, thereby allowing to combine AIMPs with arbitrary basis sets. The quality of AIMPs depends upon the quality of the reference calculation. However, to achieve the correct nodal structure of the valence orbitals the valence basis sets are larger than those required for the pseudo-orbital method and include tight GTOs.

3.4 Size-Extensivity Errors

Although the general approaches towards the inclusion of dynamical electron correlation discussed so far yield identical results going to infinite order and infinite excitation, respectively, truncated methods display shortcomings.

An important issue is the correct scaling of the correlation energy with the number of particles. The correlation energy of a system consisting of n identical non-interacting molecules should scale linearly with number of independent subsystems n. CC and MPn in fact give the correct answer. This is not generally true for truncated CI methods. A related property is size-consistency, i.e. the energy of two noninteracting systems must be the sum of the individual components.

$$E_{AB}(R_{AB} \to \infty) = E_A + E_B \quad (38)$$

A method may be size-extensive but not size-consistent. Hence, it is desirable to apply a size-extensive electron correlation method to a size-consistent reference wave function. Since RHF is not size-consistent, correlation treatments based upon RHF reference wave function may not necessarily be size-consistent at the correlated level either.

The lack of size-extensivity of truncated CI in fact renders it useless for systems containing many electrons, correct relative energies require an unbiased treatment of electron correlation throughout electronic states and molecular configurations. Owing to the lack of
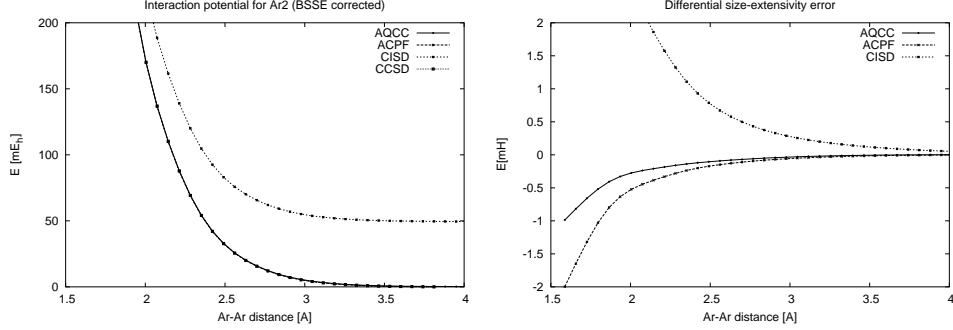
Figure 5. Ar-Ar interaction potential corrected for BSSE computed at CCSD, CISD, ACPF and AQCC level of theory using the cc-CVTZ basis set, all electrons correlated. As the basis lacks diffuse functions, the interaction potential is completely repulsive and corresponds to the closed-shell single reference case at all distances. The differential size-extensivity error defined as the difference to the CCSD energy shifted such that $\Delta E(r \to \infty) = 0$. Van der Waals radius of Ar is 1.88 Å, empirical well depth for Ar_2 is estimated to 99.7 cm^{-1} (453.6μE_h) at d=3.757Å.

generally applicable methods for multi-configurational reference wave functions, approximately size-extensive MRCI methods have been developed. The widely used a posteriori Davidson correction scales the computed correlation energy with the weight of the reference configuration in the final wave function

$$\Delta E_{Davidson} = (E - E_0)(1 - c_0^2) \tag{39}$$

where E_0 denotes the energy of the reference wave function and c_0^2 is the weight of the relaxed reference wave function in the final wave function. Alternatively, the size-extensivity of the MRCI method may be approximately restored by optimizing the renormalized functional, where Ψ^{ex} is the component of the wave function not included in the reference space (intermediate normalization).

$$E_{corr} = \frac{\langle \Psi | \mathcal{H} - E_0 | \Psi \rangle}{1 + g \langle \Psi^{ex} | \Psi^{ex} \rangle} \tag{40}$$

The scaling factor g depends upon the number of correlated electrons n_e and defines various approximations such as MRAQCC[33] ($g = 1 - \frac{(n_e - 3)(n_e - 2)}{n_e(n_e - 1)}$) and MRACPF[34] ($g = \frac{2}{n_e}$). $g = 1$ corresponds to MRCI.

Whereas a MRCI treatment is variational and does not diverge even though the reference space might be inadequate, this does not apply to the size-extensivity corrected variants. They depend upon the proper choice of the reference space and similar to MPn intruder states and near-degeneracies with configurations not included in the reference space produces artifacts. Hence, for scanning large portions of the potential energy surface MRCI though suffering from the lack of size-extensivity is more robust than MRAQCC or MRACPF.

Whereas CCSD is size-consistent, i.e. the interaction potential goes for large distances to zero, this does neither apply to CISD nor to its size-extensivity corrected counterparts (Figure 5, left) although it may be small in some cases. However, using the supermolecule

approach amounts to shifting the zero point of the potential to the Ar-Ar potential at large distances. Since the Ar_2 case is an ideal single reference case the degree of size-extensivity can be approximately judged by the difference between the CCSD and the AQCC/ACPF/CISD curves (Figure 5, right).

3.5 Orbital Resolution

The separation of MO coefficient optimization (HF or MCSCF) from the dynamical electron correlation treatment introduces a dependence upon the MO basis. The problem of orbital resolution is connected to the partitioning of the MO space. Whereas the HF energy is invariant to unitary transformation among the occupied or unoccupied orbitals this does not apply to electron correlation methods: Møller-Plesset perturbation theory requires the canonical HF orbitals, CASSCF calculations are invariant only with respect to rotations among frozen, inactive, active and virtual orbitals etc. Whereas some of the orbital dependencies (such as for MP2) are rather related to the implementation, others are inherent due to the choice of the method-dependent configuration space selection. Whenever the MO basis is partially invariant to orbital rotations in the MO optimization step they need to be "resolved" by solving an eigenvalue problem of some operator with non-degenerate eigenvalues within the invariant subspace such as a Fock matrix or the one-electron density matrix. However, accidental degeneracies may occur and if the degenerate orbitals in the subsequent electron correlation treatment are split into different orbital groups spurious results (such as spikes on a PES) may occur. The remedy is to use a different orbital resolution operator.

Regarding the computation of excitation energies by choosing the MO basis from a state-specific orbital optimization introduces a bias in favour of this state in the subsequent dynamical electron correlation treatment. This can be observed as a systematic error in the excitation energies. For this reason commonly state-averaged orbitals are employed, that is the energy functional that is minimized during orbital optimization is a weighted average over all states of interest.

Since the ground and excited state PES are quite different at different levels of theory, at certain molecular configurations we are close to avoided crossings at one level of theory while far away from it at a different level. If this occurs for the orbital optimization step in contrast to the inclusion of dynamical electron correlation, the MO basis may be even qualitatively completely wrong thereby reducing the accuracy of the subsequent electron correlation treatment drastically. To overcome this bias by inclusion of a sufficiently large configuration space requires substantial effort if at all successful.

3.6 Relativistic Effects

Relativistic effects can be defined as anything arising from the finite speed of light ($c \approx$ 137au) as compared to $c = \infty$ for the non-relativistic case. The most fundamental starting point for molecular many electron relativistic treatments is the Dirac-Breit Hamiltonian $\mathcal{H}^{DB}$ with possibly additional quantum electrodynamical corrections.

$$\mathcal{H}^{DB} = \mathcal{H}^{DC} + \mathcal{H}^{Breit} \tag{41}$$

$$= \sum_i h_i^{Dirac} + \sum_{i>j} 1/r_{ij} + \mathcal{H}^{Gaunt} + \mathcal{H}^{retard} \tag{42}$$

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$\mathcal{H}^{DB}$ can be viewed as the Dirac-Coulomb Hamiltonian $\mathcal{H}^{DC}$ plus perturbative treatment of two-electron relativistic corrections (Gaunt term and retarded Hamiltonian or derived corrections from QED). $\mathcal{H}^{DC}$ treats one-electron relativistic effects exactly in terms of a linear combination of N one-electron Dirac Hamiltonians h^{Dirac} while retaining the non-relativistic electron-electron repulsion term. The relativistic four-component single-particle wave functions can be decomposed into two two-components termed "large" and "small". These terms are related by the kinetic energy balance condition. In contrast to the non-relativistic case the Dirac-Breit Hamiltonian cannot be rigorously derived and is not fully Lorentz invariant so that purists may consider a relativist theory of many-electron systems not yet available.

The spectrum of the Dirac-Breit Hamiltonian is qualitatively characterized by having the bound states bracketed by continuum states at $-2c^2 \geq E > -\infty$ and $\infty > E \geq 0$. The presence of a negative continuum leads to the variational collapse (Brown-Ravenhall disease). Either by imposing appropriate boundary conditions or by modifying the Hamiltonian such as to project out the undesired negative continuum prevents the variational collapse (no-pair Hamiltonian[35]). Once the appropriate relativistic Hamiltonian is chosen in principle the standard non-relativistic methods can be applied analogously except for working with a four-component wave function. Expanding the large and small components in atom-centered basis sets requires very large basis sets as to fullfill the kinetic energy balance condition. This puts serious constraints upon the range of applicability so that the fully relativistic approach is often simplified by quasirelativistic approximations or the use of pseudopotentials especially since we have to consider electron correlation and relativistic effects simultaneously.

In the non-relativistic limit the small component vanishes and only the large component is retained. Separating large and small components by unitary transformations of the relativistic Hamiltonian and truncating the resulting Hamiltonian at order c^{-2} yields the Pauli and Breit-Pauli two-component form starting from $\mathcal{H}^{DC}$ and $\mathcal{H}^{DB}$, respectively. Eliminating magnetic interactions (spin-orbit coupling) only the mass-velocity correction and the Darwin term are retained.

$$\mathcal{H}_{massvel} = -\frac{1}{8c^2} \sum_i p_i^4 \tag{43}$$

$$\mathcal{H}_{Darwin} = \frac{\pi}{2c^2} \sum_{iA} \delta \mathbf{r}_{iA} \tag{44}$$

$$\tag{45}$$

Choosing instead the four-component no-pair Hamiltonian[35] as starting point and applying the Douglas-Kroll transformation[36] finally yields the spin-free relativistic one-component Douglas-Kroll Hamiltonian. The latter is variationally stable and can be employed in all-electron treatments. All-electron one-component treatments of systems containing many heavy atoms is computationally demanding due to the large size of relativistic basis sets although much cheaper than their fully relativistic counterparts. Relativistic ECPs whether of pseudopotential or AIMP type are usually derived from relativistic Cowan-Griffin[37] or Douglas-Kroll all-electron calculations. The parametrization of RECPs may also accommodate error compensation such as deficiencies in the reference data and inappropriate basis sets. Due to this empirical element they should be used only in combination with the valence basis set used for parametrization. AIMPs on the other hand may be com-

bined with any basis set sufficiently flexible to represent the nodal structure of the valence orbitals.

The main consequences of relativistic effects are (i) radial contraction of all s and $p_{1/2}$ atomic orbitals as well as the inner-shell $p_{3/2}$ AOs (ii) the spin-orbit splitting for all AOs with non-vanishing orbital angular momentum and (iii) the radial expansion and energetic destabilization of most d and all f type AOs[38]. Relativistic effects influence the chemistry of 5d block elements, lanthanoids and in particular the actinoids owing to relativistic changes to the valence shell structure. This makes them potentially offering a very rich not yet explored chemistry. Particular large effects are found for gold and gold chemistry (aurophilic attraction)[39]. Similar applies to strong closed-shell interactions, which are primarily a consequence of relativistic effects[40].

4 Extrapolation Schemes

4.1 One-Electron Basis Set Extrapolation

Of particular importance is the possibility to extrapolate to the complete basis set limit. This amounts to extrapolating horizontally to the right in Figure 2. To allow for extrapolation schemes it is mandatory to have a hierarchical sequence of basis sets that converge uniformly to the CBS limit. The cc-pVXZ, cc-pCVXZ basis sets form such a sequence. Since the HF energy and the correlation energy have different convergence characteristics separate extrapolation of each term is important.

For the correlation energy there is some theoretical motivation on the functional form establishing a relationship between maximum angular momentum of the basis set and the correlation energy ΔE_{corr} of He at the CI level and for many-electron atoms at the MP2 level. The asymptotic behaviour of the contribution by all orbitals of angular momentum l by a basis saturated individually for each l is given by

$$\Delta E_{corr,l} = a(l + \frac{1}{2})^{-4} \tag{46}$$

Given a (saturated) basis set with maximum quantum number l, the correlation energy is of the form

$$\Delta E_{corr} = \Delta E_{corr,\infty} + b(L + 1)^{-3} \tag{47}$$

Identifying $L + 1$ with the cardinal number X (D=2,T=3,...) of the cc basis sets and using a two-point extrapolation with two successive basis sets we obtain

$$\Delta E_{corr,\infty} = \frac{\Delta E_{corr,X+1}(X + 1)^3 - \Delta E_{corr,X}X^3}{(X + 1)^3 - X^3} \tag{48}$$

It has been empirically found, that the most reliable results are obtained by two-point fits using the two largest practical basis sets[23]. Comparison with correlated calculations using R12 methods indicate the correct asymptotic basis set limit for the correlation energy[42] The CBS limit of the correlation energy should be independent of the chosen pair of basis sets. In practice these authors have found that extrapolations involving the X=D basis sets are inferior. As the number of basis functions N in the basis sets grow as X^3, the correlation energy scales as $O(1/N)$ and the computational effort for integral evaluation

scales as $O(N^4)$ so that the relation between correlation energy and CPU time consumption is $\Delta E_{corr} \approx ct_{cpu}^{-4}$.

The extrapolation of the HF energy to the CBS limit has no theoretical motivation. Most popular are the exponential and power forms, e.g.

$$E_{HF} = E_{HF,\infty} + Be^{-\alpha X} \tag{49}$$

$$E_{HF} = E_{HF,\infty} + BX^{-\alpha} \tag{50}$$

$$\tag{51}$$

Apart from the general finding that the HF energy converges much more rapidly than the correlation energy with cardinal number X, conclusions are ambiguous about the extrapolation error[43].

Application of this extrapolation formula to reaction enthalpies , weak interactions[44], spectroscopic constants and dipole moments[45] have been encouraging and a statistical analysis of the extrapolated data to experimental as well as reference data based on the MP-R12[21,22] and the CC-R12 method[41] indicate that *chemical accuracy*, i.e. $\approx 4kJ/mol$ can be achieved already at the 34-extrapolation level. 23-extrapolations, though already largely improving the quality of the results compared to the raw data, are far from chemical accuracy. Similar applies to the raw data itself even for large basis sets. The exponential extrapolation advocated by Dunning and coworkers tends to overestimate the rate of convergence.

$$\Delta E_X^{corr} = E_\infty^{corr} + ae^{bX} \tag{52}$$

It is somewhat problematic that a good estimate of the CBS limit requires large basis sets thereby excluding application to large molecules. Truhlar et. al. extrapolated HF and correlation energies by the form[46]

$$E_{HF} = E_{HF,\infty} + A_{HF}X^{-\alpha} \tag{53}$$

$$E_{corr} = E_{corr,\infty} + A_{corr}X^{-\beta} \tag{54}$$

$$\tag{55}$$

The constants α and β are considered universal and have been obtained by fitting the X=D,T energies to the CBS limits estimated by larger efforts. This method allows to extrapolate to the CBS limit using relatively small basis sets[47]. However, since double zeta type basis sets are known to be insufficient for electron correlation, the parametrization must take care of it, which adds an element of statistical uncertainty as error compensation is implicitly exploited, which may or may not work on systems not included in the test suite used for parametrization.

In order to derive a basis set convergence for molecular properties, which may be largely different from the electronic energy, one starts from an expression involving the energy derivative of the Hamiltonian

$$\mathcal{H}(\lambda) = \mathcal{H}(\lambda = 0) + \lambda\mathcal{V} \tag{56}$$

so that a given property is associated with some perturbation of the Hamiltonian. Upon expanding the correlation energy as

$$E_{\lambda,X}^{corr} = \sum_{n=0}^{\infty}\sum_{k=0}^{\infty}\frac{C_n^{(k)}\lambda^k}{k!}X^{-n} \tag{57}$$

the coefficients $C_n^{(k)}$ govern the convergence of the kth order property. It is a priori not possible to predict the relative importance of the terms scaling as X^{-n}, so that asymptotic scaling may not be achieved with basis sets of cardinal numbers, for which it is possible to perform calculations and each property requires careful investigations.

A note of caution must be supplied as well: the extrapolations solely models the errors associated with the expansion of the electron-electron cusp. Other errors such as basis set superposition error, size-extensivity error or the use of an ill-chosen basis (e.g. lack of diffuse basis functions for multipole moments) must be corrected for separately. Secondly, it is necessary to point out that these extrapolation schemes have been used mostly in conjunction with single-reference systems at the MP or CC level of theory. Since the above scheme considers dynamic electron correlation only, it is tempting to extend it to multi-reference cases by defining the electron correlation energy with respect to energy of the reference wave function. However, the rather foggy distinction between dynamic and non-dynamic electron correlation and thereby its dependence upon reference configuration space definition, suggests a cautious attitude.

4.2 N-Electron Basis Set Extrapolation

Retaining a given one-electron basis somewhat similar extrapolations to the FCI limit, i.e. in vertical direction in Figure 2 would be desirable. Similar to the hierarchical one-electron basis sets, a systematic, uniform improvement of the N-electron basis is mandatory. Møller-Plesset perturbation series can be ruled out due to the tendency to diverge at high order without having an a priori error indicator at hand. Truncated approximately size-extensive MRCI cannot be easily extended in practical terms. Thus, coupled-cluster methods seem to provide the only possible route to this task. Truncating the cluster operator $\mathcal{T}$ heavily such as e.g. in CCD, CC2 may yield extrapolations largely benefitting from error compensation (such as e.g. MP2). CCSD(T) and CCSDT, however, already come quite close to the FCI limit and continuing to higher order cluster expansions may allow accurate extrapolations. Due to the introduction of new techniques CC codes capable of going to high order truncations of the cluster operator may become available in near future.

4.3 Gaussian-n (Gn) Models

In actual problems, however, the ultimate aim is to extrapolate to the FCI result at CBS limit (i.e. the exact result) including corrections for zero-point vibration and relativistic effects as to model the experimental situation, i.e. extrapolation to the upper right corner of Figure 2. Although effects due to one- and N-electron basis set truncation are in general non-additive, extrapolation models can be devised, which assume the additivity of certain contributions. As the model is devised such as to reproduce the data (energies, ionization potentials, electron affinities, proton affinities) of a test suite of molecules, by virtue of the choice of basis sets and level of correlation treatment, error compensation is implicitly made use of. The G3 model[50] uses a HF/6-31G(d) optimized equilibrium structure and scaled harmonic frequencies (scale factor 0.8929) to compute the zero-point energy. The geometry is refined at the all-electron MP2/6-31G(d) level. A series of single-point calculations is carried out at this molecular geometry to estimate the correlation energy starting with an MP4/6-31G(d) calculation as reference point. Corrections are computed for diffuse

functions, higher polarization functions, correlation contributions beyond MP4 through quadratic CI (a CC variant) and corrections for basis set effects and non-additivity of diffuse vs. polarization function extensions computed at all-electron MP2 level. Spin-orbit corrections for atomic species taken from experiment or accurate theoretical calculations are added along with the zero point energy. Finally, so-called higher level corrections - a parametrized expression depending upon the number of valence electron pairs optimized to reproduce the test suite results - are added. Average deviations for energies, ionization potentials, electron affinities, proton affinities are between 4 and 8 kJ/mol. The Gn models (n=1,2,3)[48–50] are available for first and second row elements, only. Moreover, due to assuming additivity for various contributions and parametrized higher level correction this model is likely to benefit largely from error compensation, so that it would be difficult to extend it to the entire periodic table. There are also variants G2(MP2)[51] and G3(MP2)[52], which estimate basis set effects at MP2 level. The associated computational effort goes as G3(MP2)<G2(MP2)<G3<G2[52]. Note in particular, that the Gn methods are tied to certain basis sets and targets, for which these basis sets are inadequate will invariably lead to unreliable results.

5   Calibration and Reference Data

A remarkable side effect of extrapolation schemes parametrized to fit experimental data (thereby relying on error compensation) is the availability of extensive test suites of molecules, for which reliable experimental data or accurate data from other sources exist. This includes e.g. the G(n) test sets[49] . There are many such reference data concerning a variety of properties frequently used for parametrization of density functionals. Although the agreement with the reference data may be stunning regarding the comparatively small effort, they constitute unbounded extrapolation for systems not included in the test suite. In addition error estimates are unavailable as the implicit error compensation may add up effects of opposite sign, which in turn depend upon the system in question. Large discrepancies between such extrapolations and the experimental data may indicate experimental errors as well as a failure of the extrapolation procedure as well.

More reliable calibration procedures avoid tying themselves to experimental data but rather invoke a sequence of calculations of increasing accuracy in terms of one- and N-electron basis sets, chosen to allow separating the various errors and judging to what extent additivity is a safe assumption.

A considerable problem associated with quantum chemical calculation comprises the decision whether a given method is applicable to a given problem. In many cases there is no simple a priori yes/no answer to the problem but instead a series of test calculations is required. Solely comparing the computed results with some experimental or otherwise derived reference data is frequently of little help, since we cannot distinguish between error compensation and correct results. In other words even despite of good agreement with reference data, we cannot connect it to the parameters determining the outcome of the quantum chemical calculations. In addition, we face the problem of having either no reference data at hand or the derivation of the reference data themselves relied on theoretical models that may not be appropriate. Thus multiple sources of error generally hamper any reasonable interpretation of the comparison.

Therefore, a generally profitable approach is to perform *series* of quantum chemical

calculations, which are set up such as to deduce the effect of a single source of error as accurately as possible. Since it is not save to assume straightforwardly the additivity of different error sources calibration or benchmarking certain sources of error against a judicial chosen reference is of great value for the understanding on the properties of quantum chemical methods. In particular systematic investigations on the impact of certain parameters, provide a considerable insight into the methods and are to some extent transferable.

Of crucial importance is to disentangle the one-electron basis set truncation error from the intrinsic (i.e. systematic) error of a given method. Since it is usually not possible to repeat extensive calibration calculations for large molecules, it is sensible to define a set of representative reference molecules. Setting up a series of calculations we aim at elucidating the intrinsic (or systematic) error of quantum chemical methods with respect to the desired property. Provided, the reference set was chosen appropriately, the results will be mostly transferable to the larger systems.

Of particular value are benchmarks probing the full N-electron basis set limit within a given (incomplete) one-electron basis. Here FCI calculations are to be mentioned in the first place - as they are exact within the given one-electron basis set, which should be of double zeta if possible triple zeta quality for meaningful comparisons. Second to it are coupled-cluster techniques including quadruple or higher excitations in particular the R12 variants, which converge rapidly to the one-electron basis set limit. At least for true single-reference cases they practically reproduce the FCI data . For the general case and small molecules size-extensivity corrected MR-SDCI such as MR-AQCC and MR-ACPF may provide reference data. Often it is necessary to extrapolate to the CBS limit in the course of the analysis.

5.1 Error Indicators

Hence, scrutinizing solely the final results of a series of calculations will indicate the non-applicability of a given method by divergence or convergence to different method-dependent limits. To understand the failure of a method requires to verify whether the basic assumptions of the method hold for the specific case.

Provided the MOs are obtained from a qualitatively correct SCF calculation it is still the question for diagnostics on the applicability of the method. In case of CI one can simply examine the weight of the reference wave function: if configurations with large weights appear from outside the reference space, the reference space must be appropriately adjusted. For Coupled-Cluster methods commonly the $\mathcal{T}_1$ diagnostic is used, which amounts to the scaled norm of the single excitation cluster amplitudes. The reasoning for the choice of this indicator is that the single excitations reflect orbital bias best. CCSD calculations with $\mathcal{T}_1 > 0.02$ call for caution; inclusion of higher excitations will increase the robustness of the CC treatment. Møller-Plesset perturbation theory is less effective. Looking at the norm of correction vector and energy of MP2 solely may erroneously indicate applicability. Including MP3 and monitoring the change in correlation energy increment and norm of the correction vector is more sensitive and more representative of the convergence of the MPn series. The approximately size-extensively corrected MRCI functionals such as MRACPF and MRAQCC are also fairly sensitive to intruder states, which in serious cases may force them to diverge (this depends upon the wave function optimization scheme).

Finally, Figure 6 displays the characteristic behaviour of various standard techniques on the dissociation of the N_2 molecule. Note, that methods relying on the closed shell
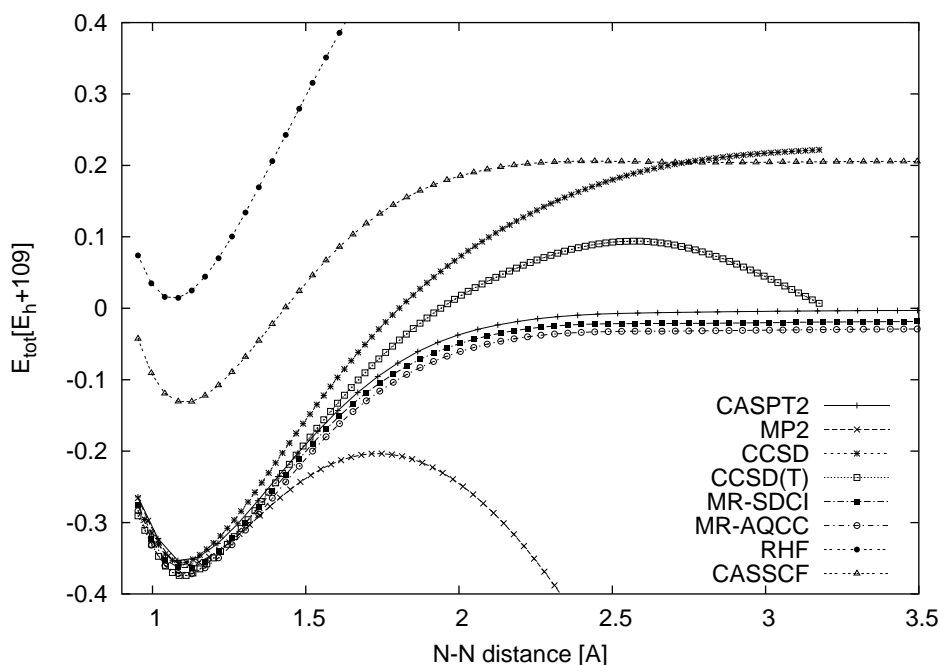
Figure 6. Total energies computed at various levels of theory: RHF, CASSCF (valence CAS, 176 CSFs), MP2, CCSD, CCSD(T), CASPT2 (valence CAS), MR-CISD (valence CAS reference space), MR-AQCC (valenc CAS reference space); cc-pVTZ basis set, 1s electrons kept frozen; experimental dissociation energy 0.364 E_h and bond length 1.074 Å.

HF reference (MP2, CCSD, CCSD(T)) fail badly as the RHF reference performs poorly. Methods relying on an appropriate zeroth order MCSCF reference wave functions (MR-CISD, MRAQCC, CASPT2) describe the dissociation qualitatively correct.

6 Summary

This brief survey has described the most relevant ingredients and practical error sources in quantum chemical (cluster) calculations using standard quantum chemical methods such as HF, MCSCF, perturbation theory, coupled-cluster methods and configuration interaction. It has been pointed out that the most important error sources are, apart from using a single-reference method in a multi-reference case, the choice of one- and N-electron basis set. The concept of non-dynamical versus dynamical electron correlation has been explained. The molecular orbital basis may give rise to a bias in favour of one state or be even qualitatively completely inadequate for a given purpose. Improving the MO basis is much more important than high-level electron correlation treatment. Orbital rotations mixing MOs that are treated on a different footing in the dynamical correlation treatment lead to artifacts. Relativistic effects are important for the chemistry of the heavy elements. However, even for the second and third-row elements relativistic effects have to be considered for highly accurate calculations. Highly accurate data can be obtained only from extrapolations to

the CBS limit, high-level electron correlation treatment and elimination of size-extensivity and BSSE errors.

Cheap extrapolation models aiming at the applicability to a wide range of systems almost invariably contain an element of statistics, which ties the model explicitly and/or implicitly to a set of reference data thereby benefitting from error compensation.

A critical attitude towards the quality of a calculation is very beneficial. Decomposition of the total error into its various sources and calibration of some suitably chosen reference systems should always be taken into account whenever there is some fundamental doubt about the results given the required level of accuracy.

Acknowledgments

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