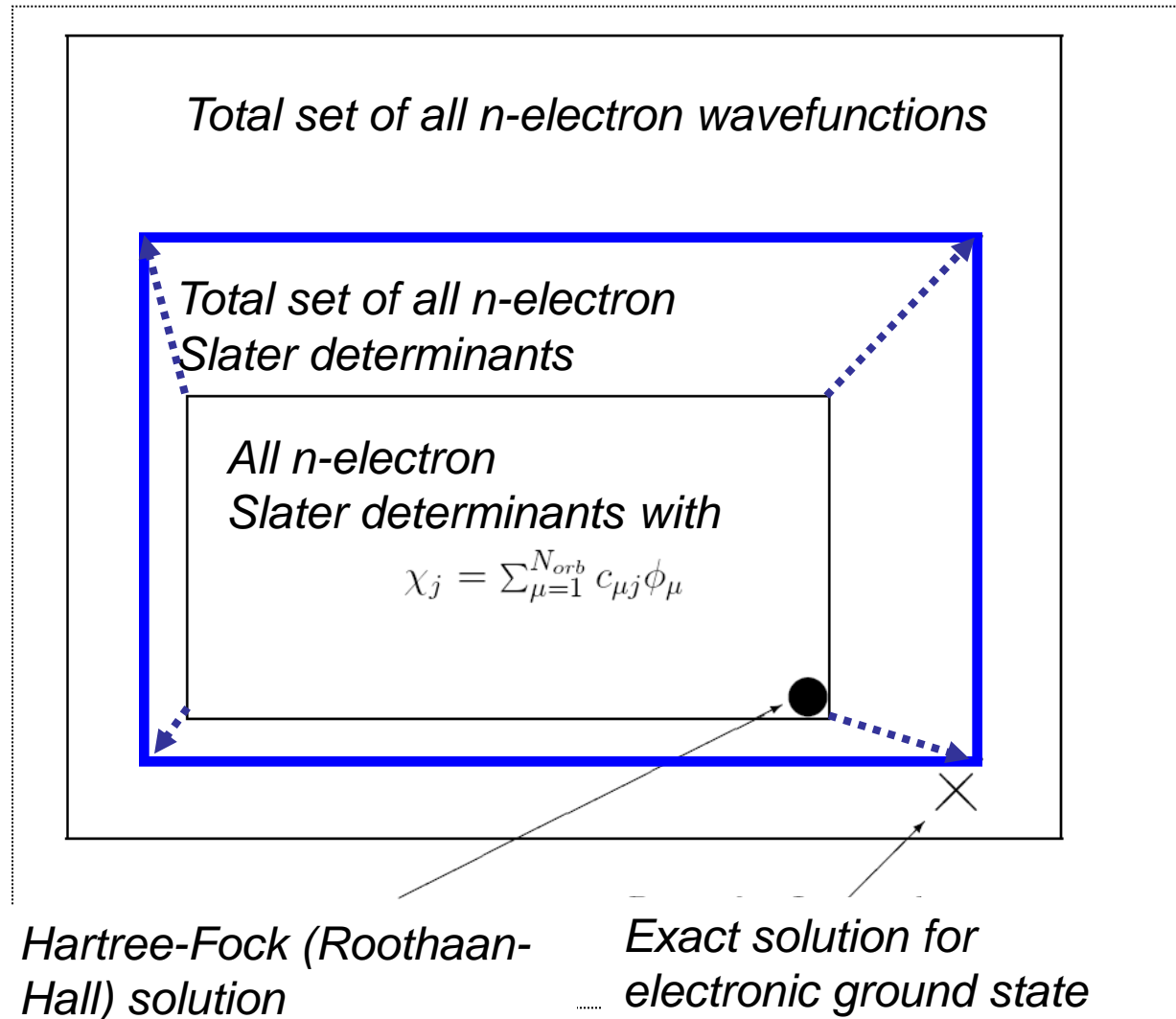


Principle of Hartree-Fock calculation

We need to get beyond the Hartree-Fock limit



How can we make a wavefunction outside the blue frame?

Substituted determinants(I)

This is the HF determinant which has occupied orbitals only

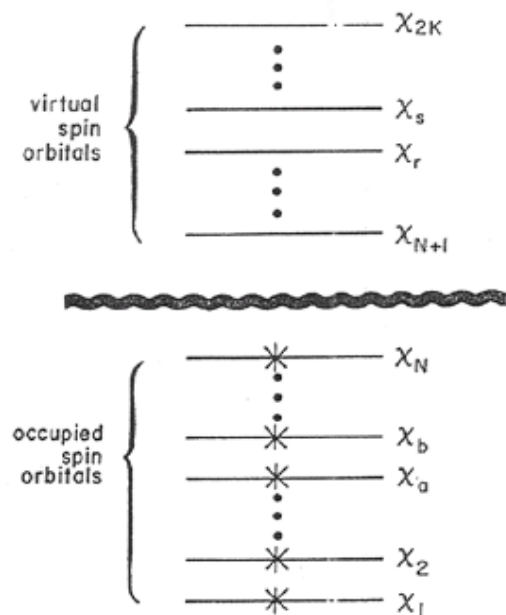
$$\Psi_0^{(\text{HF})}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \xi_1) & \psi_2(\mathbf{r}_1, \xi_1) & \dots & \psi_j(\mathbf{r}_1, \xi_1) & \dots & \psi_n(\mathbf{r}_1, \xi_1) \\ \psi_1(\mathbf{r}_2, \xi_2) & \psi_2(\mathbf{r}_2, \xi_2) & \dots & \psi_j(\mathbf{r}_2, \xi_2) & \dots & \psi_n(\mathbf{r}_2, \xi_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_n, \xi_n) & \psi_2(\mathbf{r}_n, \xi_n) & \dots & \psi_j(\mathbf{r}_n, \xi_n) & \dots & \psi_n(\mathbf{r}_n, \xi_n) \end{vmatrix}.$$

This is a *singly substituted determinant*

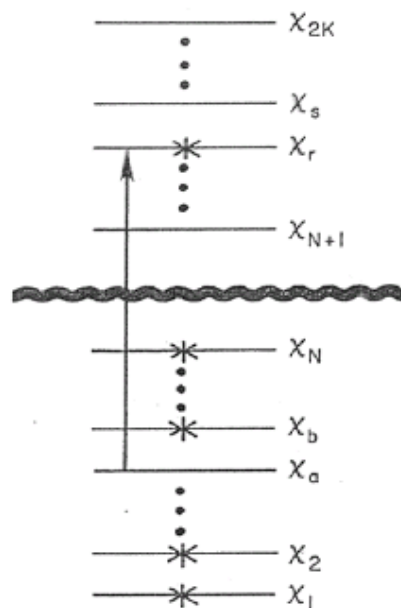
$$\Psi_j^a(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \xi_1) & \psi_2(\mathbf{r}_1, \xi_1) & \dots & \psi_a(\mathbf{r}_1, \xi_1) & \dots & \psi_n(\mathbf{r}_1, \xi_1) \\ \psi_1(\mathbf{r}_2, \xi_2) & \psi_2(\mathbf{r}_2, \xi_2) & \dots & \psi_a(\mathbf{r}_2, \xi_2) & \dots & \psi_n(\mathbf{r}_2, \xi_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_n, \xi_n) & \psi_2(\mathbf{r}_n, \xi_n) & \dots & \psi_a(\mathbf{r}_n, \xi_n) & \dots & \psi_n(\mathbf{r}_n, \xi_n) \end{vmatrix}.$$

ψ_j is an occupied orbital; ψ_a is a virtual orbital

Illustrations of ground state and substituted determinants



$$|\Psi_a^r\rangle$$



$$|\Psi_{ab}^{rs}\rangle$$

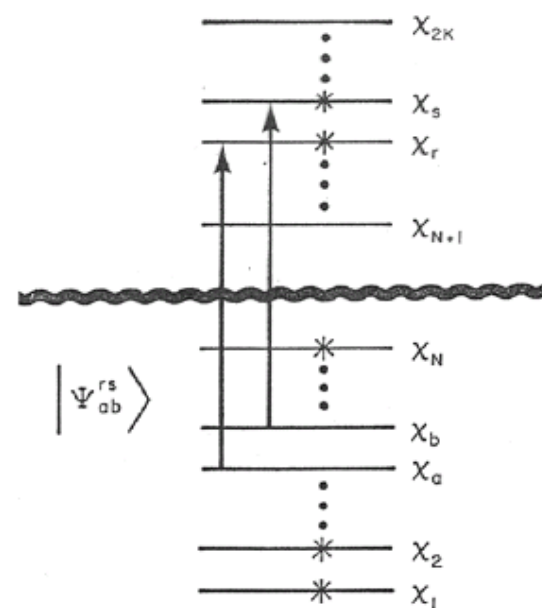


Figure 2.4 The Hartree-Fock ground state determinant, $|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$.

Figure 2.7 A singly excited determinant.

Figure 2.8 A doubly excited determinant.

Beyond the Hartree-Fock calculation

To improve the approximation for the wavefunction, we make the new “Ansatz”

$$\Psi_0^{(\text{CI})} = a_{00}\Psi_0^{(\text{HF})} + \sum_{s>0} a_{s0}\Psi_s^{(\text{HF})}$$

Hartree-Fock determinant

(selected) substituted determinants

Expansion coefficients to be determined by matrix diagonalization

This is the principle of a CI (configuration interaction) calculation. The unknown wavefunction is a linear combination of known basis functions (substituted determinants). This leads to matrix diagonalization as always in theoretical chemistry....

Perturbation theory: fundamentals (I)

For a perturbation theory treatment of electron correlation we need a definition of the **unperturbed system** to begin with.

It is obvious to choose the **Hartree-Fock wavefunction** Ψ_0 of the ground state as the unperturbed wavefunction. Ψ_0 is an eigenfunction of the operator

$$(8) \quad \hat{H}^{(0)} = \sum_{i=1}^N \hat{F}(i)$$

$$(9) \quad \hat{H}^{(0)}\Psi_0 = E_0^{(0)}\Psi_0$$

$$(10) \quad E_0^{(0)} = \sum_{a=1}^N \varepsilon_a$$

Eqs. (8)-(10) define the **unperturbed operator** $\hat{H}^{(0)}$ and the associated **unperturbed energy** $E_0^{(0)}$ of the ground state (making use of spin orbitals).

Perturbation theory: fundamentals (II)

The perturbation \hat{V} reads:

$$(11) \quad \hat{V} = \hat{H} - \hat{H}^{(0)} = \sum_{i=1}^N \hat{h}(i) + \sum_{i=1}^N \sum_{j=2}^N \frac{e^2}{r_{ij}} - \sum_{i=1}^N \hat{F}(i)$$

$$(12) \quad \hat{V} = \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{r_{ij}} - \sum_{i=1}^N \sum_{b=1}^N [\hat{J}_b(i) - \hat{K}_b(i)]$$

This corresponds to the difference between the true (real) Coulomb repulsion of the electrons and the averaged repulsion in the Hartree-Fock model. The definitions (8)-(12) underlie the **Møller-Plesset (MP) perturbation theory**.

Second-order perturbation theory: MP2 (I)

Application of the general perturbation theory formulas:

$$(13) \quad E_0^{(2)} = \sum_{n \neq 0} \frac{|V_{0n}|^2}{E_0^{(0)} - E_n^{(0)}}$$

In principle, the sum runs over all excited determinants (or configurations). However, only the **double-excitations** contribute because only these interact directly with the Hartree-Fock ground state. Only the two-electron terms in the perturbation (12) make non-vanishing contributions to the corresponding matrix elements V_{0n} ; these contributions are known:

$$(14) \quad E_0^{(2)} = \sum_{a < b} \sum_{r < s} \frac{|\langle ab || rs \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Second-order perturbation theory: MP2 (II)

The restricted summation ($a < b, r < s$) makes sure that any double-excitation $ab \rightarrow rs$ from occupied into unoccupied spin orbitals appears only once (alternative formulation: no restrictions and a prefactor $1/4$).

The energy denominators are differences of the corresponding orbital energies (negative: $\varepsilon_a, \varepsilon_b < \varepsilon_r, \varepsilon_s$).

$E_0^{(2)}$ is a sum of **contributions from each electron pair** (first-order pair energies e_{ab}^{FO}):

$$(15) \quad E_0^{(2)} = \sum_{a < b} \sum_{r < s} e_{ab}^{\text{FO}}$$

$$(16) \quad e_{ab}^{\text{FO}} = \sum_{r < s} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

CC: the exponential ansatz (I)

Formal ansatz (fundamental equation) for the coupled-cluster wavefunction:

$$(17) \quad \Phi_0 = \exp(\hat{T})\Psi_0$$

The excitation operator (cluster operator) \hat{T} acts on the Hartree-Fock wavefunction Ψ_0 . It contains terms for all possible excitations (one-, two-, ..., N -particle excitations):

$$(18) \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N$$

CC: the exponential ansatz (II)

The operators \hat{T}_p are defined using creation and annihilation operators (in the language of second quantization). Their operation on Ψ_0 yields the corresponding p-fold excitations including the associated amplitudes:

$$(19) \quad \hat{T}_1 \Psi_0 = \sum_a \sum_r t_a^r \Psi_a^r$$

$$(20) \quad \hat{T}_2 \Psi_0 = \sum_a \sum_{b>a} \sum_r \sum_{s>r} t_{ab}^{rs} \Psi_{ab}^{rs}$$

$$(21) \quad \hat{T}_3 \Psi_0 = \sum_a \sum_{b>a} \sum_{c>b} \sum_r \sum_{s>r} \sum_{t>s} t_{abc}^{rst} \Psi_{abc}^{rst}$$

CC: the exponential ansatz (III)

The exponential function of an operator is defined by the corresponding Taylor-series expansion:

$$(22) \exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \dots$$

$$(23) \exp(\hat{T}) = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 + \dots$$

Approximations:

$$(24) \hat{T} = \hat{T}_2 \quad \text{CCD}$$

$$(25) \hat{T} = \hat{T}_1 + \hat{T}_2 \quad \text{CCSD}$$

$$(26) \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \quad \text{CCSDT}$$

Multi-reference methods (I)

There are cases where a single configuration (e.g. the Hartree-Fock determinant) is not capable of describing a system qualitatively correctly, because other configurations of comparable energy exist.

Examples:

- dissociation of covalent bonds
- transition states in chemical reactions
- electronically excited states
- transition metal atoms (configurations $d^n s^2$, $d^{n+1} s$, d^{n+2}) and related transition metal compounds

In such cases **multi-configuration** approaches are required in order to include **static correlation** and to describe the system qualitatively correctly.

Multi-reference methods (II)

MCSCF: Multiconfigurational Self-Consistent Field.

Basic idea: The qualitatively important configurations are selected. In the MC wavefunction all linear parameters (i.e., the CI coefficients and the LCAO-MO coefficients) are optimized variationally. Thus, the orbitals are the optimum for the chosen MC wavefunction, and they can differ significantly from single-determinant orbitals.

Problem: The selection of the “important” configurations is arbitrary up to a certain extent. Systematization:

CASSCF: Complete Active Space Self-Consistent Field

For the chosen active orbitals all configurations are taken into account (full CI in the active space).

Potential curves for H₂: SCF vs. MCSCF

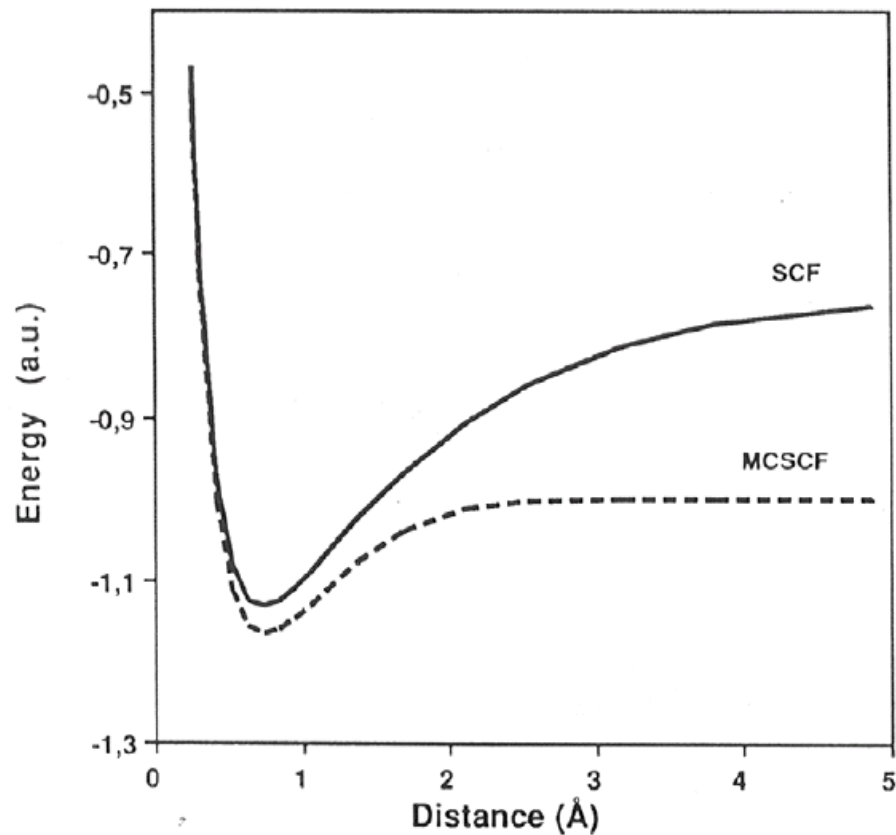


Figure 2.1 Potential curves for H₂ showing the erratic behaviour of the SCF curve as a function of the internuclear distance. For comparison the MCSCF curve which dissociates correctly is also given.

Multi-reference methods (III)

CASPT2: A CASSCF calculation with a few active orbitals does consider only the static correlation. To include the **dynamical correlation**, a second-order perturbation theory calculation is carried out in CASPT2 using CASSCF as the reference wavefunction. This approach has proven to be successful in many applications.

MRCI: In multi-reference CI approaches the qualitatively important configurations are selected (in analogy to MCSCF) as reference configurations (typically about 2-10), and then all single and double excitations are included in the CI expansion. Relative to a given reference configuration, multiple excitations (e.g. quadruple excitations) are taken into account. Therefore, MRCI is a method which includes the most important higher configurations in the framework of a CISD model, and thus approaches the FCI limit.

Multi-reference methods (IV)

CASSCF-CI: MRCI (typically with single and double excitations) for a CASSCF reference wavefunction.

Classification: MRCI and CASSCF-CI are expensive and powerful methods to describe electron correlation in “difficult” multi-reference systems.

Ab initio methods: Philosophy

Ab initio methods aim at the exact solution of the non-relativistic Schrödinger equation.

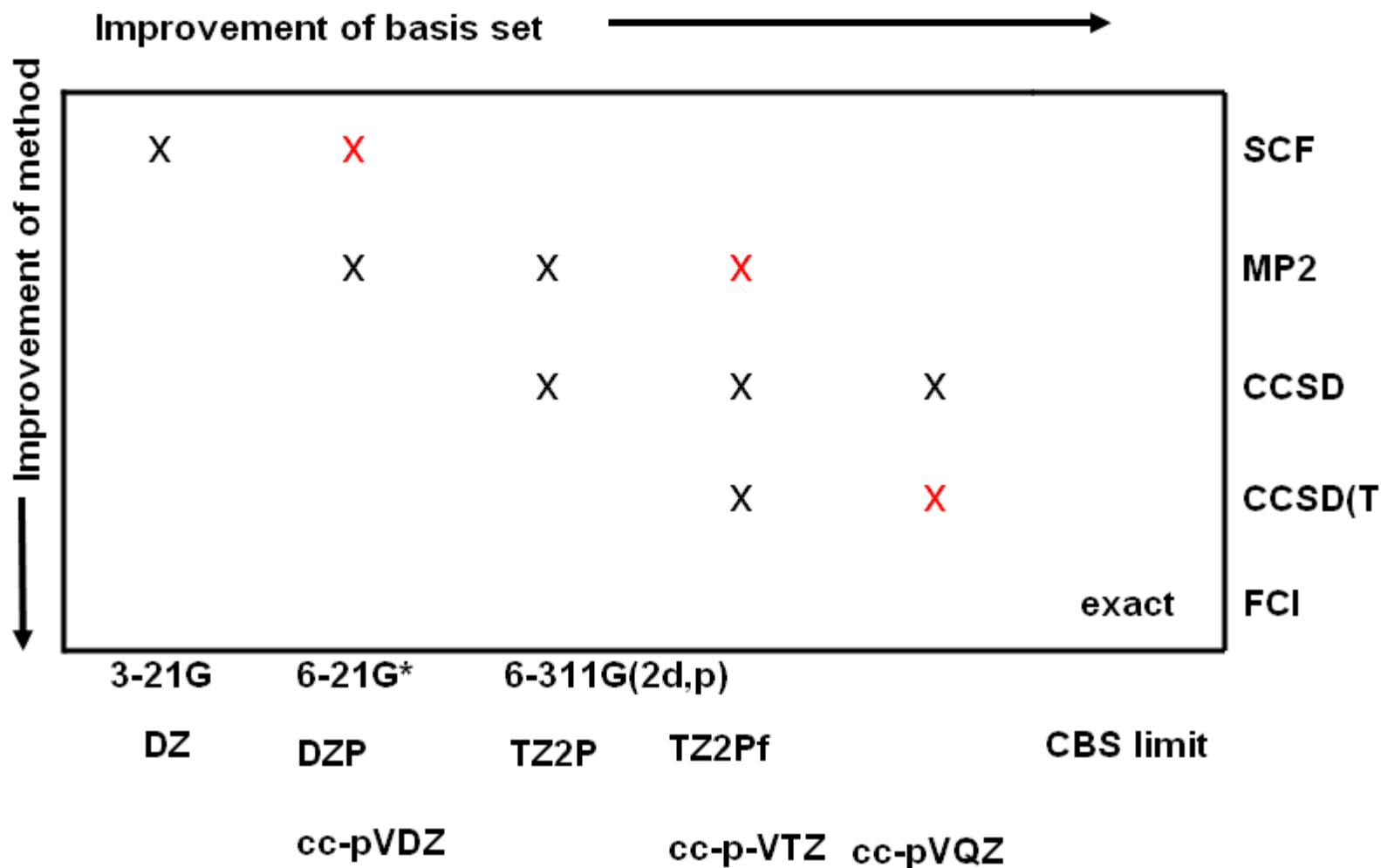
They provide a convergent path to this exact solution which is approached in a systematic manner by proper choice of

- the one-particle basis for the wave function
- and the N-particle basis for the correlation treatment.

Acronyms:

- RHF Restricted Hartree-Fock
- MP2 Second-order Møller-Plesset perturbation theory
- CCSD Coupled cluster theory with single and double excitations
- CCSD(T) CCSD with perturbational triples treatment
- FCI Full configuration interaction

Survey of ab initio treatments



Recommended: SCF/DZP, MP2/TZ2Pf, CCSD(T)/cc-pVQZ

***The Born-
Oppenheimer
Approximation***

Nuclear-motion calculation

$$\hat{H}_N(\mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R})$$

from *ab initio* calculation



$$\hat{H}_N(\mathbf{R})\chi_m(\mathbf{R}) = E\chi_m(\mathbf{R})$$

„observable“ energy



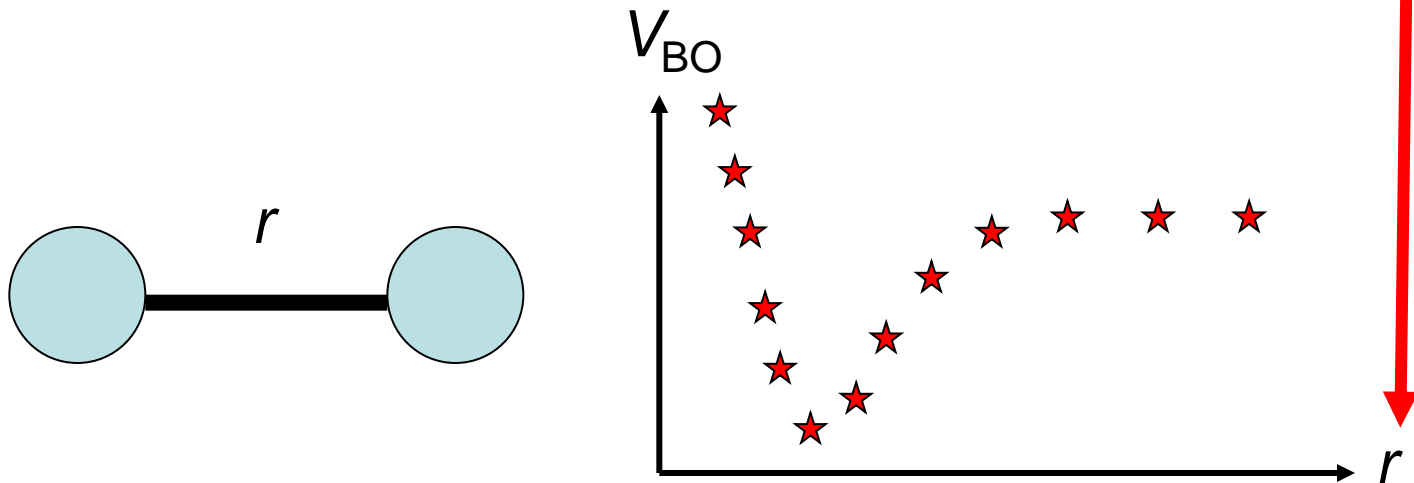
The solution of the nuclear-motion Schrödinger equation is an important job of the theoretical spectroscopist

Ab initio (electronic structure) calculation

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r})$$

nuclear positions fixed in space

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$



***In practice:
convert Schrödinger
equation to matrix
eigenvalue equation***

***Diagonalize matrix with
computer***

Basis functions?

$$\Psi_k = \sum_{j=1}^n c_{jk} \phi_j$$

How do we choose these basis functions?

Wavefunctions and expansion coefficients are initially unknown – the basis functions must be chosen.

Rotation-vibration problem:

Basis of eigenfunctions for „model“ molecule:

- *Rigidly rotating molecule*
- *Harmonically vibrating molecule*

„Nuclear“ Schrödinger equation?

$$\hat{H}_n \psi_n(\mathbf{R}_n) = E_{ne} \psi_n(\mathbf{R}_n)$$

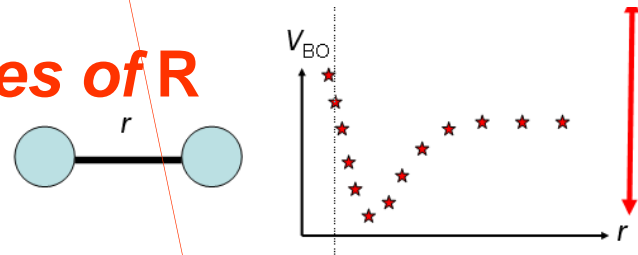
Initial approximation

$$\psi_n(\mathbf{R}_n) \approx \psi_{\text{vib}}(\mathbf{R}_{\text{vib}}) \psi_{\text{rot}}(\mathbf{R}_{\text{rot}})$$

So we need to solve two Schrödinger equations:

(i)
$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$

must be solved for many values of R



(ii)
$$\hat{H}_{\text{N}}(\mathbf{R}) = \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R}) \quad \hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

$$\hat{H}_{\text{N}}(\mathbf{R})\chi_m(\mathbf{R}) = E\chi_m(\mathbf{R})$$

must only be solved once.