Exact and Approximate Wave Functions

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Characteristics of Exact Wave Function

Time-independent non-relativistic **Schrödinger equation**

$$\widehat{H}\Psi(x_1,\ldots,x_n) = E\Psi(x_1,\ldots,x_n)$$

$$x_1 = (r_1, \sigma_1)$$

Composite coordinate for spatial and spin degree of freedom

Hamiltonian in coordinate representation

$$\widehat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I}{r_{iI}} + \sum_{i<j}^{n}\frac{1}{r_{ij}}$$

In practice, it is difficult to solve the Schrödinger equation as the WF describes the **correlated motion** of N electrons.

The exact wavefunction is also an eigenfunction of any operator that commutes with the Hamiltonian:

If $\widehat{H}\Psi = E\Psi$ and $\widehat{A}\Psi = a\Psi$ then $\left[\widehat{H}, \widehat{A}\right] = 0$

Exact conditions on the electronic wave function

1. **Antisymmetric** to permutation of any pair of electrons

   $$P_{ij}\Psi = -\Psi$$

2. **Square-integrable** and hence normalizable for the bound state

   $$\langle\Psi|\Psi\rangle = 1$$

3. **Molecular point group symmetry** is obeyed

   $$\widehat{O}\,\Psi = o\Psi$$

   Spatial symmetry: enforce the same spatial symmetry by expanding the WF in the symmetry-adapted orbitals.

4. Eigenfunction of **total and projected spin operators**

   $$S^2\Psi = S(S+1)\Psi$$

   Spin symmetry: correct spin behavior may be enforced by expanding the WF in the symmetry-adapted linear combinations determinants (CSFs).

   $$S_z\Psi = M\Psi$$
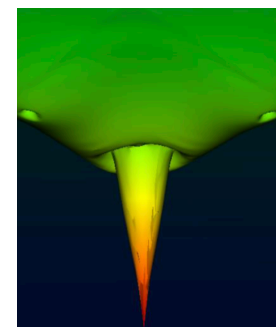
Exact conditions on the electronic wave function

5. Exact WF is **variational** in the sense that for all possible variations δΨ, which are orthogonal to the wave function, the energy remains unchanged:

$$\langle \delta\Psi | \Psi \rangle = 0 \Rightarrow \langle \delta\Psi | H | \Psi \rangle = 0$$

6. Exact WF must possess a characteristic non-differentiable behavior for spatially coinciding electrons, known as the **electronic Coulomb cusp condition.**

7. Exact WF must possess a characteristic non-differentiable behavior for electrons coinciding point-like nuclei, known as the **nuclear cusp condition.**

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{Z_1}{r} + \hat{R} - E_k \right) \left(\Psi_k(\mathbf{x})\big|_{r=0} + r\frac{\partial \Psi_k(\mathbf{x})}{\partial r}\bigg|_{r=0} + \ldots \right) = 0$$

$$\frac{\partial \Psi(\mathbf{x})}{\partial r}\bigg|_{r=0} = -Z\Psi(\mathbf{x})\big|_{r=0}$$

Exact conditions on the electronic wave function

8. Exact WF is **size-extensive**; for a system containing **non-interacting subsystems** the total energy is equal to the sum of the energies of the individual systems.

$$H_T = \sum_{i=1}^{M} H_i \qquad H_T \Psi_T = E_T \Psi_T \qquad E_T = \sum_{i=1}^{M} E_i \qquad H_i \Psi_i = E_i \Psi_i$$

9. Exact WF decays at large distances the electron density decays as

$$\rho(r) \sim \exp(-2^{3/2}\sqrt{I}r),$$

where I is the ionization potential of the molecule.

10. Exact WF transforms in a characteristic manner under **gauge transformations** of the potentials associated with electromagnetic fields, ensuring that all molecular properties described by the wave function are unaffected by the transformations.

Approximating the electronic wave function

Popular Strategy: Seek for the approximate solution to the Schrödinger equation numerically by expanding the unknown function in a finite linear combination of known functions.

$$|C> = \sum_i^m C_i |i> \qquad\qquad E(\mathbf{C}) = \frac{\langle \mathbf{C}| \widehat{H} |\mathbf{C}\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle}$$

The Schrödinger equation becomes a matrix generalized eigenvalue equation

1. In the limit of a **complete set** of orbitals, the **exact solution** to the Schrödinger equation arrives.
2. The chosen basis should be **tractable**, in the sense that the Hamiltonian and overlap matrices can be evaluated.
3. The chosen basis should be **suitable** in the sense that accurate approximations can be obtained with few terms.

Variational Principle

According to the variation principle, the solution of the TI Schrödinger equation is equivalent to an optimization of the energy functional:

$$E(\mathbf{C}) = \frac{\left\langle \mathbf{C} \mid \widehat{H} \mid \mathbf{C} \right\rangle}{\langle \mathbf{C} \mid \mathbf{C} \rangle}$$

- It provides a simple and powerful procedure for generating approximate wave functions.
- The **stationary points** of energy function are the **approximate electronic states** $|C>$, and the values $E(C)$ at the stationary points are the **approximate energies**.

In order to locate and to characterize the stationary points, we shall employ the first and second derivatives with respect to the variational parameters:

$$E_i^{(1)}(\mathbf{C}) = \frac{\partial E(\mathbf{C})}{\partial C_i} \qquad \text{Electronic Gradient}$$

$$E_{ij}^{(2)}(\mathbf{C}) = \frac{\partial^2 E(\mathbf{C})}{\partial C_i \partial C_j} \qquad \text{Electronic Hessian}$$

Electronic energy derivatives

$$E(\mathbf{C})\langle \mathbf{C} | \mathbf{C} \rangle = \left\langle \mathbf{C} | \widehat{H} | \mathbf{C} \right\rangle \qquad |\mathbf{C}> = \sum_{i}^{m} C_i |i>$$

Exercise: obtain the gradient and Hessian elements.

$$
\begin{aligned}
E_i^{(1)}(\mathbf{C}) &= \frac{\partial E(\mathbf{C})}{\partial C_i} = 2\frac{\langle i | \hat{H} | \mathbf{C} \rangle - E(\mathbf{C}) \langle i | \mathbf{C} \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle} \\
E_{ij}^{(2)}(\mathbf{C}) &= \frac{\partial^2 E(\mathbf{C})}{\partial C_i \partial C_j} = 2\frac{\langle i | \hat{H} | j \rangle - E(\mathbf{C}) \langle i | j \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle} - 2E_i^{(1)}(\mathbf{C})\frac{\langle j | \mathbf{C} \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle} - 2E_j^{(1)}(\mathbf{C})\frac{\langle i | \mathbf{C} \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle},
\end{aligned}
$$

Electronic Gradient

The condition for stationary points:

$$E_i^{(1)}(\mathbf{C}) = 0 \qquad 2\frac{\langle i|\hat{H}|\mathbf{C}\rangle - E(\mathbf{C})\langle i|\mathbf{C}\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle} = 0 \qquad \text{then} \qquad \langle i|\hat{H}|\mathbf{C}\rangle = E(\mathbf{C})\langle i|\mathbf{C}\rangle$$

In matrix notation:

$$\mathbf{HC} = E(\mathbf{C})\mathbf{SC} \qquad H_{ij} = \langle i|\hat{H}|j\rangle \qquad S_{ij} = \langle i|j\rangle$$

Assuming antisymmetric N-electron function are orthogonal: $\qquad \delta_{ij} = \langle i|j\rangle$

Standard **m-dimensional** eigenvalue problem: $\qquad \mathbf{HC} = E(\mathbf{C})\mathbf{C}$

This equation has exactly **m orthonormal solutions** with associated real eigenvalues:

$$\mathbf{C}_K = \begin{pmatrix} C_{1K} \\ C_{2K} \\ \vdots \\ C_{mk} \end{pmatrix} \qquad E_K = E(\mathbf{C}_K) \qquad E_1 \leq E_1 \leq \cdots \leq E_m$$

Electronic Hessian

At stationary points, the electronic Hessian elements are:

$$E_{ij}^{(2)}(\mathbf{C}) = \frac{\partial^2 E(\mathbf{C})}{\partial C_i \partial C_j} = 2\frac{\langle i|\hat{H}|j\rangle - E(\mathbf{C})\langle i|j\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle} - 2E_i^{(1)}(\mathbf{C})\frac{\langle j|\mathbf{C}\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle} - 2E_j^{(1)}(\mathbf{C})\frac{\langle i|\mathbf{C}\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle},$$

$$^{K}E_{ij}^{(2)} = E_{ij}^{(2)}(\mathbf{C}_K) = 2\left(\left\langle i|\widehat{H}|j\right\rangle - E_K\langle i|j\rangle\right)$$

At stationary point gradient vanish and eigenvectors are normalized.

Hessian in the basis of eigenvectors of Hamiltonian:

$$^{K}E_{MN}^{(2)} = 2\left(\left\langle M|\widehat{H}|N\right\rangle - E_K\langle M|N\rangle\right) = 2(E_M - E_K)\delta_{MN}$$

$$^{K}E_{MM}^{(2)} = 2(E_M - E_K)$$

Correspond to the excitation energies (multiplied by 2) for the transition from $|K\rangle$ to $|M\rangle$).

Hylleraas-Undheim Theorem

In the linear variation method, the **Kth eigenvalue will always drop** as the variational space is extended, providing a highly systematic way of approaching the exact state.

$$\delta = \dim S'' - \dim S'$$

two linear variational spaces $S' \subset S''$

$$E''_K \leq E'_K \leq E''_{K+\delta}$$

The vector space is systematically extended and generates a sequence of energies that converge monotonically from above towards the exact energies.

Five lowest eigenvalues of ${}^1\Sigma^+$ of BH

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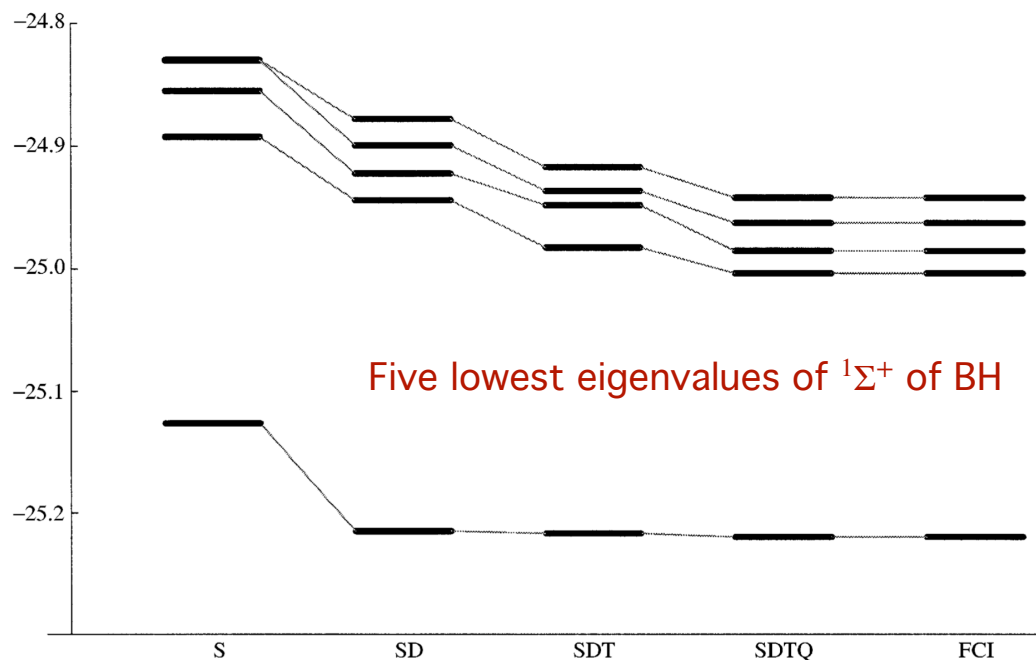
Derivatives and Properties

– **Responses to geometrical perturbations**

  ‣ Forces and force contacts

  ‣ Spectroscopic constants

– **Responses to external electromagnetic fields**

  ‣ Permanent and induced moments

  ‣ Polarizabilities, magnetizabilities and optical activity

– **Responses to external magnetic fields and nuclear magnetic moments**

  ‣ NMR shielding and indirect spin–spin coupling constants

  ‣ EPR hyperfine coupling constants and g values

Electronic Energy Function

When a molecular system is perturbed, its total energy changes

$$\mathcal{E}(\mu) = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}\mu + \tfrac{1}{2}\mathcal{E}^{(2)}\mu^2 + \cdots$$

When the perturbation is static (time-independent), the properties may be calculated by differentiation

$$\mathcal{E}^{(1)} = \left.\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\mu}\right|_{\mu=0}$$ First-order molecular properties (dipole moments and gradients)

$$\mathcal{E}^{(2)} = \left.\frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}\mu^2}\right|_{\mu=0}$$ Second-order molecular properties (polarizabilities and Hessians)

Numerical differentiation (finite differences and polynomial fitting)

Analytical differentiation (derivatives calculated from analytical expressions)

Electronic Energy Function

The electronic energy function contains the Hamiltonian and the wave function:

$$E(\mu, \mathbf{C}) = \left\langle \mathbf{C} \,|\, \widehat{H}(\mu) \,|\, \mathbf{C} \right\rangle$$

It depends on two distinct sets of parameters:

μ : **external** (perturbation) parameters (geometry, external field)

$\mathbf{C}$: **electronic** (wave-function) parameters (MOs, cluster amplitudes)

$$\widehat{H}(\mu) = \hat{h}(\mu) + \hat{g}(\mu) + \hat{h}_{nuc}(\mu)$$

$$\widehat{H}(\mu) = \sum_{pq} h_{pq}(\mu) E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs}(\mu) e_{pqrs} + h_{nuc}(\mu)$$

$$\hat{h}(\mu) = \left\langle \Phi_p(\mu) \,|\, h_{pq}(\mu) \,|\, \Phi_q(\mu) \right\rangle$$

➡ Hamiltonian depends **explicitly** on the external parameters

➡ Wave function depends **implicitly** on the external parameter

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Electronic Energy and its Derivatives

The electronic energy $\varepsilon(\mu)$ is obtained by optimizing the energy function $E(\mu, \mathbf{C})$ for $\mathbf{C}$ for each value of μ.

$$\varepsilon(\mu) = E(\mu, \mathbf{C}')$$

note: the optimization is not necessarily a variational minimization

Calculate the derivative of $\varepsilon(\mu)$ with respect to μ:

$$\frac{d\varepsilon(\mu)}{d\mu} = \underbrace{\frac{\partial E(\mu, \mathbf{C}')}{\partial \mu}}_{\text{explicit dependence}} + \underbrace{\frac{\partial E(\mu, \mathbf{C})}{\partial \mathbf{C}}\Big|_{C=C'}\frac{\partial \mathbf{C}}{\partial \mu}\Big|_{C=C'}}_{\text{implicit dependence}}$$

$\dfrac{\partial \mathbf{C}}{\partial \mu}$ is the **wavefunction response** and tells us how the electronic structure changes when the system is perturbed.

Variational and nonvariational wave functions

- Variational wave functions:

  The optimized energy fulfills the **stationary (variational) condition:**

  $$\frac{\partial E(\mu, \mathbf{C})}{\partial \mathbf{C}} = 0 \qquad \text{(for all } \mu\text{)}$$

  where μ is the geometry and $\mathbf{C}$ the electronic parameters.

  The stationary condition determines $\mathbf{C}$ as a function of the geometry $\mathbf{C}(\mu)$

- Nonvariational wave functions:

  wave functions whose energy does not fulfill the stationary condition

Examples of Variational and Nonvariational wave functions

$$\frac{\partial E_{SCF}(\mu, \kappa)}{\partial \kappa_{ia}} = 0$$

Hartree–Fock energies variational in an unconstrained exponential (orbital-rotation) parametrization ($|HF> = exp(-\kappa)|0>$)

$$\frac{\partial E_{SCF}(\mu, C)}{\partial C_{\mu i}} \neq 0$$

Hartree–Fock energies nonvariational in a constrained LCAO parametrization.

$$\frac{\partial E_{MCSCF}}{\partial C_{\mu i}} \neq 0$$ respect to MO coefficient

$$\frac{\partial E_{MCSCF}}{\partial c_i} \neq 0$$ respect to CI coefficient

$$\frac{\partial E_{CI}}{\partial \kappa_{ia}} \neq 0$$

$$\frac{\partial E_{CI}}{\partial c_i} \neq 0$$

$$\frac{\partial E_{FCI}}{\partial c_i} = 0$$ respect to CI coefficient

respect to MO coefficient

$$|FCI> = \sum_i c_i |i>$$

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Molecular Gradients

The total derivative of the energy, applying the chain run:

$$\frac{d\varepsilon(\mu)}{d\mu} = \frac{\partial E(\mu, \mathbf{C})}{\partial \mu} + \frac{\partial E(\mu, \mathbf{C})}{\partial \mathbf{C}} \frac{\partial \mathbf{C}}{\partial \mu}$$

Invoke the **stationary condition**:

$$\frac{\partial E(\mu, \mathbf{C})}{\partial \mathbf{C}} = 0$$ Zero electronic gradient

The molecular gradient then simplifies to:

$$\frac{d\varepsilon(\mu)}{d\mu} = \frac{\partial E(\mu, \mathbf{C})}{\partial \mu}$$

For variational wave functions, we do not need the response of the wave function $\frac{\partial \mathbf{C}}{\partial \mu}$ to calculate the molecular gradient.

The Hellmann–Feynman theorem

Assume that the (stationary) energy is an expectation value: :

$$E(\mu, \mathbf{C}) = \left\langle \mathbf{C} \,|\, \widehat{H}(\mu) \,|\, \mathbf{C} \right\rangle$$

$$\frac{d\varepsilon(\mu)}{d\mu} = \frac{\partial E(\mu, \mathbf{C})}{\partial \mu} = \left\langle \mathbf{C}' \,|\, \frac{\partial \widehat{H}}{\partial \mu} \,|\, \mathbf{C}' \right\rangle \qquad \leftarrow \text{the Hellmann–Feynman theorem}$$

Relationship to **first-order perturbation theory:** $\qquad E^{(1)} = \left\langle \mathbf{0} \,|\, H^{(1)} \,|\, \mathbf{0} \right\rangle$

Example for geometrical distortions: $\qquad \dfrac{d\varepsilon}{d\mathbf{R}_K} = - \left\langle C \,|\, \displaystyle\sum_i \frac{Z_K r_{iK}}{r_{ik}^3} \,|\, C \right\rangle + \displaystyle\sum_{I \neq K} \frac{Z_I Z_K R_{IK}}{R_{IK}^3}$

Classical interpretation: integration over the force operator

Molecular Hessians for Variational Wave Functions

Differentiating the molecular gradient, we obtain the molecular Hessian

$$\frac{d^2\varepsilon}{d\mu^2} = \frac{d}{d\mu}\frac{\partial E(\mu,\mathbf{C})}{\partial\mu} = \left(\frac{\partial}{\partial\mu} + \frac{\partial\mathbf{C}}{\partial\mu}\frac{\partial}{\partial\mathbf{C}}\right)\frac{\partial E(\mu,\mathbf{C})}{\partial\mu}$$

$$= \frac{\partial^2 E(\mu,\mathbf{C})}{\partial^2\mu} + \frac{\partial^2 E(\mu,\mathbf{C})}{\partial\mu\partial\mathbf{C}}\frac{\partial\mathbf{C}}{\partial\mu}$$

To obtain the molecular Hessian we need the first order response (not second order), and to determine the response we differentiate the stationary condition:

To determine the response, we differentiate the stationary condition:

$$\frac{\partial E(\mu,\mathbf{C})}{\partial\mathbf{C}} = 0 \qquad \frac{\partial}{\partial\mu}\frac{\partial E(\mu,\mathbf{C})}{\partial\mathbf{C}} = \frac{\partial^2 E}{\partial\mu\partial\mathbf{C}} + \frac{\partial^2 E}{\partial^2\mathbf{C}}\frac{\partial\mathbf{C}}{\partial\mu} = 0 \qquad \frac{\partial^2 E}{\partial^2\mathbf{C}}\frac{\partial\mathbf{C}}{\partial\mu} = -\frac{\partial^2 E}{\partial\mu\partial\mathbf{C}}$$

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Molecular Hessians for Variational Wave Functions

electronic
Hessian

$$\frac{\partial^2 E}{\partial^2 \mathbf{C}} \cdot \frac{\partial \mathbf{C}}{\partial \mu} = -\frac{\partial^2 E}{\partial \mu \partial \mathbf{C}}$$

perturb electronic
gradient

- the electronic Hessian is independent of the perturbation
- its dimensions are usually large and it cannot be constructed explicitly
- the response equations are usually solved by iterative techniques

Analogy with Hooke's law:

force constant→ $\quad k\mathbf{x} = -F \quad$ ← force

the wave function relaxes by an amount proportional to the perturbation

For molecular gradients and Hessians, we have the expressions

$$\frac{d\varepsilon(\mu)}{d\mu} = \frac{\partial E(\mu, \mathbf{C})}{\partial \mu}$$ ← zero-order response needed

$$\frac{\partial^2 \varepsilon}{\partial \mu^2} = \frac{\partial^2 E(\mu, \mathbf{C})}{\partial^2 \mu} + \frac{\partial^2 E(\mu, \mathbf{C})}{\partial \mu \partial \mathbf{C}} \frac{\partial \mathbf{C}}{\partial \mu}$$ ← first-order response needed

For variational wave functions, the derivatives of the wave function to order n determine the energy derivatives to order 2n + 1.

Derivatives and Properties

$\dfrac{\partial E}{\partial \mathbf{R}_i}$	Force on its nucleus	$\dfrac{\partial E}{\partial \mathbf{F}}$	Dipole moment vector
$\dfrac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$	Quadratic force constant, harmonic vibrational frequencies	$\dfrac{\partial^2 E}{\partial \mathbf{F}^2}$	Electric polarizability tensor
$\dfrac{\partial^4 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j \partial \mathbf{R}_k \partial \mathbf{R}_l}$	Quartic force constant, anharmonicties	$\dfrac{\partial^3 E}{\partial \mathbf{F}^3}$	First polarizability tensor

Derivatives and Properties

$\dfrac{\partial^2 E}{\partial \mathbf{F} \partial \mathbf{R}_i}$	Dipole moment derivatives, infrared intensities	$\dfrac{\partial E}{\partial \mathbf{B}}$	Magnetic dipole moment vector
$\dfrac{\partial^3 E}{\partial \mathbf{F}^2 \partial \mathbf{R}_i}$	Electric polarizability derivatives, Raman scattering intensities	$\dfrac{\partial^2 E}{\partial \mathbf{B}^2}$	Magnetizability tensor
$\dfrac{\partial^3 E}{\partial \mathbf{F} \partial \mathbf{R}_i \partial \mathbf{R}_j}$	Electrical anharmonicity, vibrational overtone intensities	$\dfrac{\partial E}{\partial \mathbf{m}_A}$	Spin density on nucleus A