TCC Electronic Structure Module
L1: Exact and inexact wavefunctions

David P. Tew

February 7, 2021

Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

L1 Exact and inexact wavefunctions

L2 Hartree–Fock theory

L3 Configuration Interaction theory

L4 Møller–Plesset perturbation theory

L5 Coupled-cluster theory

L6 Properties and excited states

L7 Density Functional Theory

L8 Density Functional Approximations

Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

1 Introduction

Theoretical chemistry is the discipline of constructing and using physical models to explain and predict phenomena observed in chemical systems. The equations of quantum mechanics provide an extremely powerful physical model that contains all of the fundamental physics that govern the behaviour of the electrons and nuclei that make up a chemical system. The equations are in general too complex to be solved analytically, but they can be solved approximately using numerical techniques and with the help of computers. However, it is not possible perform simulations to evolve the quantum state of a system with arbitrary numbers of particles and we must make decisions concerning what to include in a simulation and what can be safely ignored. Even a perfectly accurate numerical simulation will always be an idealised model of reality.

In the broader context of theoretical chemistry, electronic structure theory is primarily concerned with a specific question: what are the eigenstates of the electronic wavefunction for a given position of a chosen set of nuclei? The answer to this question can be used to directly probe structure and bonding in molecular systems and to predict properties such as multipoles, ionisation energies and electron affinities. The information from the electronic energy and wavefunction can also be combined with theoretical models to treat the kinetics or thermodynamics of the nuclear motions to compute reaction energies, rate constants, spectroscopic signatures involving transitions between quantum states, and much more.

These lectures are concerned with the theory used to solve the time-independent non-relativistic Schrödinger equation for n electrons in the electrostatic field of a chosen set of N nuclei at positions $\mathbf{R}_I$ and with charges Z_I.

$$\hat{H}\Psi_k(\mathbf{x}_1, \ldots, \mathbf{x}_n) = E_k \Psi_k(\mathbf{x}_1, \ldots, \mathbf{x}_n) \tag{1}$$

where k labels the quantum state with energy E_k and $\mathbf{x}_1$ is a composite coordinate $(\mathbf{r}_1, \sigma_1) = (x_1, y_1, z_1, \sigma_1)$ for the spatial and spin degrees of freedom. The Hamiltonian for the electronic wavefunction is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N} \frac{(Z_I e)\, e}{4\pi\epsilon_0\, r_{iI}} + \sum_{i<j}^{n} \frac{e^2}{4\pi\epsilon_0\, r_{ij}} \tag{2}$$

where e is the electronic charge; m_e the electronic mass; ϵ_0 the vacuum permitivity; r_{iI} the separation of electron i and nucleus I; r_{ij} the separation of electrons i and j. It is convenient to use atomic units where $\hbar = 4\pi\epsilon_0 = m_e = e = 1$ so that

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N} \frac{Z_I}{r_{iI}} + \sum_{i<j}^{n} \frac{1}{r_{ij}} \tag{3}$$

Let us first examine some formal aspects of the electronic Schrödinger equation.

2 Exact conditions on the electronic wavefunction

Exact condition 1

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

$$\text{If} \quad \hat{H}\Psi = E\Psi \quad \text{and} \quad [\hat{H}, \hat{A}] = 0, \quad \text{then} \quad \hat{A}\Psi = a\Psi. \tag{4}$$

In particular, since electrons are Fermions and $\hat{H}$ is independent of spin and is invariant to permutations among electron coordinates and among nuclear coordinates, then

- Fermionic antisymmetry is obeyed $\hat{\pi}_\mu \Psi = (-1)^{p_\mu}\Psi$
- Spin is a good quantum number $\hat{S}^2\Psi = S(S+1)\Psi$
- Spin polarisation is a good quantum number $\hat{S}_z\Psi = M_s\Psi$
- Molecular point group symmetry is obeyed $\hat{O}\Psi = o\Psi$

Exact condition 2

The local energy is a constant, equal to the eigenstate energy everywhere in space

$$E_{\text{loc}}(\mathbf{x}) \equiv \frac{\hat{H}\Psi_k(\mathbf{x})}{\Psi_k(\mathbf{x})} = E_k \tag{5}$$

Note that this holds at points infinitesimally close to nodal surfaces where $\Psi_k(\mathbf{x}) = 0$ and therefore also on the nodal surfaces.

Exact condition 3

Condition 2, together with the requirement that the wavefunction is finite and continuous, has the consequence that the divergences in the Coulombic interaction that occur at all points where charged particles coalesce, must be exactly cancelled by an equal and opposite divergence in the kinetic energy. The kinetic energy operator involves the second derivative with respect to electron position and diverges if there is a discontinuity in the first derivative. The exact wavefunction must contain these derivative discontinuities, the characteristic of which are different at coalescence of electrons with nuclei or electron-electron coalescence.

electron-nucleus coalescence: re-writing the Schrödinger equation, collecting all Hamiltonian terms that do not involve electron 1 or nucleus 1 into $\hat{R}$, gives

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z_1}{|\mathbf{R}_1 - \mathbf{r}_1|} + \hat{R}\right)\Psi_k(\mathbf{x}) = E_k\Psi_k(\mathbf{x}) \tag{6}$$

Expanding in spherical polar coordinates about the point where $\mathbf{r}_1 = \mathbf{R}_1$ and examining only the spherically symmetric terms, we obtain

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{Z_1}{r} + \hat{R} - E_k\right)\left(\Psi_k(\mathbf{x})\big|_{r=0} + r\frac{\partial\Psi_k(\mathbf{x})}{\partial r}\Big|_{r=0} + \ldots\right) = 0 \tag{7}$$

Equating powers of r and equating terms leads to Kato's cusp condition, which holds for all eigenstates k and therefore for all admissible wavefunctions

$$\left.\frac{\partial\Psi(\mathbf{x})}{\partial r}\right|_{r=0} = -Z\Psi(\mathbf{x})\big|_{r=0} \tag{8}$$

Exercise 1
The $1s$ orbital of a hydrogenic atom is $\psi(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}}e^{-Zr}$. Show that this orbital obeys Kato's cusp condition. Sketch this orbital along the z axis passing through the origin and identify the cusp. Evaluate $\partial\psi/\partial z$ at $(0, 0, +\delta)$ and $(0, 0, -\delta)$ in the limit δ goes to zero.
Exercise 2
The $2p_z$ orbital of a hydrogenic atom is $\psi(\mathbf{r}) = \sqrt{\frac{Z^5}{32\pi}}r\cos\theta e^{-Zr}$. Sketch this orbital along the z axis passing through the origin. Why does this orbital not have a cusp at electron-nucleus coalescence? Show that this orbital obeys the second-order derivative discontinuity

$$\left.\frac{\partial^2\Psi(\mathbf{x})}{\partial r^2}\right|_{r=0} = -Z\left.\frac{\partial\Psi(\mathbf{x})}{\partial r}\right|_{r=0}$$

---

electron-electron coalescence: repeating the procedure for electron-nucleus coalescence, but using sum and difference coordinates to expand about the point of coalescence for electrons 1 and 2, yeilds Kato's cusp condition for electron-electron coalescence

$$\left.\frac{\partial\Psi(\mathbf{x})}{\partial r}\right|_{r_{12}=0} = \frac{1}{2}\Psi(\mathbf{x})\big|_{r_{12}=0} \tag{9}$$

The positive sign arises because the particles are repelling rather than attracting (with unit charge) and the factor half arises from the reduced mass of the coalescing electrons.

Exact condition 4

Consider the regions where one electron is far away from the molecular framework and the rest are close. The ground state wave function is then an antisymmetrised product of that of the ground state cation and a distant electron

$$\Psi(\mathbf{x}) = \hat{\mathcal{A}}[\Psi^e(\mathbf{x}_1)\Psi^{M^+}(\mathbf{x}_2 \ldots \mathbf{x}_n)] \tag{10}$$

The local energy is the sum of the energies of the cation and the distant electron

$$E = E^e + E^{M^+} \qquad \text{so} \quad E^e = E_{\text{IP}} \tag{11}$$

where E_{IP} is the ionisation energy $E - E^{M^+}$. The long-range behaviour of $\Psi^e(\mathbf{x})$ is therefore that of a hydrogen-like 1s orbital with effective charge $\sqrt{2E_{\text{IP}}}$

$$\Psi^e(\mathbf{x}) \to e^{-\sqrt{2E_{\text{IP}}}r} \tag{12}$$

3 Approximating the electronic wavefunction

The wavefunction can be approximated numerically by expanding the unknown function in a finite basis of known functions.

$$\Psi_k(\mathbf{x}) = \sum_I f_I(\mathbf{x}) C_{Ik} \tag{13}$$

The Schrödinger equation is thus projected onto the finite Hilbert space spanned by the basis and becomes a matrix generalised eigenvalue equation

$$\sum_J H_{IJ} C_{Jk} = \sum_J S_{IJ} C_{Jk} E_k \tag{14}$$

$$H_{IJ} = \langle f_I | \hat{H} | f_J \rangle \tag{15}$$

$$S_{IJ} = \langle f_I | f_J \rangle \tag{16}$$

The chosen basis should be

a) Complete, in the sense that by systematically increasing the basis size, the approximation approaches the exact solution arbitrarily closely

b) Suitable, in the sense that accurate approximations can be obtained with few terms

c) Tractable, in the sense that the Hamiltonian and overlap matrices can be evaluated

The functions f_I are n-electron basis functions. A natural choice for f_I is a product of n 1-electron functions, draw from a set of 1-electron basis functions.

$$f_I(\mathbf{x}) = \prod_i^n f_{I_i}(\mathbf{x}_i) \tag{17}$$

The Hilbert space spanned by the n-electron functions f_I is the direct product of the n 1-electron Hilbert spaces, the size of each of which is defined by the number of 1-electron basis functions, which must be the same for every electron because they are indistinguishable particles. In the limit that the 1-electron basis is complete, the n-electron basis is also complete.

The variational principle allows us to optimise any parameters of the approximate ground state wavefunction by minimising the Rayleigh–Ritz energy

$$E \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{18}$$

This can be used to determine the linear coefficients C_I and, if desired, any non-linear parameters in the basis functions f_I. It is not common practice to optimise non-linear parameters because the Hamiltonian matrix elements must be re-evaluated after every change of basis.

When selecting the basis, we can chose either to provide a sufficiently flexible set of functions and admit errors in known exact conditions that reduce as the basis nears completeness, or impose the exact conditions on the wavefunction by imposing the conditions on each basis function. Different choices are made for the different exact conditions, depending on the severity of the approximation.

Let us first consider one-electron functions. The exact solutions for hydrogenic ions (H, He$^+$, Li^{2+} etc) are well known and are hyrdogenic orbitals $1s, 2s, 2p, 3s, 3p, 3d$ etc, and are characterised by shell structure with radial nodes and degeneracies determined by angular momentum. The exact solution to the molecular hydrogen cation H_2^+ was also determined early in the 20th century. It was found that the solutions resembled hydrogenic orbitals in the regions where the electron was close to either nucleus, and that viewing the orbital for the chemical bond as a perturbation to the states of the individual atoms provided a rapidly converging series expansion.

Thus the most common strategy for approximating one-electron states (orbitals) of molecular systems is to expand them as a linear combination of atomic orbitals (LCAO). The hyrdogenic atomic orbitals are an inconvenient set to use because a) they are only complete if the continuum states are included b) the integrals for the Hamiltonian matrix cannot be evaluated straightforwardly. Instead, the atomic orbitals are products of Gaussian radial functions and spherical harmonics, chosen to mimic hydrogenic orbitals. This expansion is complete for atoms and overcomplete for molecules and the Hamiltonian matrix elements can be evaluated analytically. By systematically adding more Gaussian atomic functions with a wider and tighter mesh of exponents, and with higher-order spherical harmonics, more flexibility is provided to the expansion to more closely reproduce the shape of the molecular orbitals. Note that the atom-centred Gaussian functions do not obey the electron-nucleus cusp conditions, but the expansion can fit the electron-nucleus cusp to arbitrary precision by including functions with ever larger exponents. It is straightforward to impose point group symmetry on the LCAO coefficients such that the molecular orbitals, and consequently the n-electron products of orbitals transform according to an irreducible representation of the molecular point group.

Turning now to the n-electron functions, the exact conditions to be considered are Fermi-antisymmetry, spin quantum numbers and the electron-electron cusp conditions. Both Fermi-antisymmetry and spin coupling introduce strong correlation among the electrons (more details in L3) and the importance of these conditions is such that they are applied on each of the n-electron basis functions (more details in L2). The electron-electron cusp introduces a much weaker correlation among the electrons (more details in L3) and this condition is not usually imposed, and is recovered in the limit of an infinite basis.