

Chapter 2

Basic Principles of quantum mechanics

For a repetition of quantum mechanics you may find the following links useful:

http://en.wikipedia.org/wiki/Quantum_mechanics

<http://ocw.mit.edu/OcwWeb/Chemistry/index.htm>

<http://ocw.mit.edu/OcwWeb/Physics/index.htm>

<http://bethe.cornell.edu/>

<http://plato.stanford.edu/entries/qm>

2.1 Postulates of Quantum Mechanics

- Postulate 1. The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends on the coordinates of all particles \mathbf{r} and on time. This function, called the wave function or state function, has the important property that $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau$ is the probability that the particle lies in the volume element $d\tau$ located at \mathbf{r} at time t . The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the probability of finding it somewhere in space is 1, so that we have the normalization condition

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau = 1 \quad (2.1)$$

It is customary to also normalize many-particle wavefunctions to 1. The wavefunction must also be single-valued, continuous, and finite.

- Postulate 2. To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics. If we require that the expectation value of an operator \hat{A} is real, then \hat{A} must

be a Hermitian operator. Some common operators occurring in quantum mechanics are collected in the following table.

Name of Observable	Symbol of Observable	Symbol of Operator	Operator
Position in 1D	x	\hat{x}	Multiply by x
Position in 3D	\mathbf{r}	\hat{r}	Multiply by \mathbf{r}
Momentum in 1D	p	\hat{p}_x	$-i\hbar \partial / \partial x$
Momentum in 3D	\mathbf{p}	\hat{p}	$-i\hbar \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right)$
Kinetic energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	\hat{H}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r})$
Angular momentum: x- component	l_x	\hat{l}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
Angular momentum: y- component	l_y	\hat{l}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
Angular momentum: z- component	l_z	\hat{l}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

Figure 2.1: Physical observables and their corresponding quantum operators (from wikipedia).

- Postulate 3. In any measurement of the observable associated with operator \hat{A} , the only values that will ever be observed are the eigenvalues a , which satisfy the eigenvalue equation

$$\hat{A}\Psi(\mathbf{r}, t) = a\Psi(\mathbf{r}, t) \quad (2.2)$$

This postulate captures the central point of quantum mechanics—the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states). If the system is in an eigenstate of \hat{A} with a single eigenvalue a , then any measurement of the quantity A will yield a .

Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of \hat{A} initially. An arbitrary state can

be expanded in the complete set of eigenvectors of \hat{A} ($\hat{A}\Psi_i(\mathbf{r}, t) = a_i\Psi_i(\mathbf{r}, t)$) as

$$\Psi(\mathbf{r}, t) = \sum_{i=1}^N c_i \Psi_i(\mathbf{r}, t) \quad (2.3)$$

where N may go to infinity. In this case we only know that the measurement of A will yield one of the values a_i , but we don't know which one. However, we do know the probability that eigenvalue a_i will occur: it is the absolute value squared of the coefficient, $|c_i|^2$, leading to the fourth postulate below.

An important second half of the third postulate is that, after measurement of Ψ yields some eigenvalue a_i , the wavefunction immediately "collapses" into the corresponding eigenstate Ψ_i . Thus, measurement affects the state of the system. This fact is used in many elaborate experimental tests of quantum mechanics.

- Postulate 4. If a system is in a state described by a normalized wavefunction Ψ , then the expectation value of the observable corresponding to \hat{A} is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) d\tau \quad (2.4)$$

- Postulate 5. The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \quad (2.5)$$

The central equation of quantum mechanics must be accepted as a postulate.

- Postulate 6. The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion¹ with those of another. Electronic spin must be included in this set of coordinates. The Pauli exclusion principle is a direct result of this antisymmetry principle. We will later see that Slater determinants provide a convenient means of enforcing this property on electronic wavefunctions.

2.2 The molecular Hamiltonian and the Born-Oppenheimer approximation

This chapter was adapted from the lecture notes "A Short Summary of Quantum Chemistry", MITOPENCOURSEWARE, December 2004.

¹Fermions: particles with half-integer spins. Electrons are fermions.
Bosons: particles with integer spin, e.g. the nucleus of a C-12 atom.

Quantum Chemistry is (typically) based on the non-relativistic Schrödinger equation within the Born-Oppenheimer approximation. The Schrödinger equation is (we use atomic units: $\hbar = 1, m_{elec} = 1, e_{elec} = 1$)

$$\hat{H}_{tot}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) \Psi_{tot}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) = E(\mathbf{R}, \mathbf{P}) \Psi_{tot}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) \quad (2.6)$$

where $\mathbf{r}, \mathbf{p} = \partial/\partial\mathbf{r}$ are the electronic collective coordinates and $\mathbf{R}, \mathbf{P} = \partial/\partial\mathbf{R}$ are the nuclear collective coordinates, and

- E is an allowed energy of the system (the system is usually a molecule).
- Ψ_{tot} is a function of the positions of all the electrons and nuclei (we drop all spin dependencies).
- \hat{H}_{tot} is a differential operator constructed from the classical Hamiltonian $H(\mathbf{P}, \mathbf{R}, \mathbf{p}, \mathbf{r}) = E$ by replacing all the momenta \mathbf{p}_i (resp. \mathbf{P}_I) with $(i)\partial/\partial\mathbf{r}_i$ ($(i)\partial/\partial\mathbf{R}_i$) as long as all the \mathbf{p} (\mathbf{P}) and \mathbf{r} (\mathbf{R}) are Cartesian.

For a system of nuclei and electrons in vacuum with no external fields, neglecting magnetic interactions, using atomic units:

$$\hat{H}_{tot} = -\frac{1}{2} \sum_I \frac{1}{M_I} \nabla_I^2 - \frac{1}{2} \sum_n \nabla_n^2 + \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{In} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_n|} + \sum_{n < m} \frac{1}{|\mathbf{r}_m - \mathbf{r}_n|} \quad (2.7)$$

The Born-Oppenheimer approximation is to neglect some of the terms coupling the electrons and nuclei, so one can write:

$$\Psi_{tot}(\mathbf{R}, \mathbf{r}) = \Psi_{nucl}(\mathbf{R}) \Psi_{elec}(\mathbf{r}; \mathbf{R}) \quad (2.8)$$

and

$$\hat{H}_{tot} = \hat{T}_{nucl}(\mathbf{P}, \mathbf{R}) + \hat{H}_{elec}(\mathbf{p}, \mathbf{r}; \mathbf{R}) \quad (2.9)$$

which ignores the dependence of \hat{H}_{elec} on the momenta of the nuclei \mathbf{P} . One can then solve the Schrödinger equation for the electrons (with the nuclei fixed, indicated by $(; \mathbf{R})$). The energy we compute will depend on the positions \mathbf{R} of those fixed nuclei, call it $E(\mathbf{R})$:

$$\hat{H}_{elec}(\mathbf{p}, \mathbf{r}; \mathbf{R}) \Psi_{elec}(\mathbf{r}; \mathbf{R}) = E(\mathbf{R}) \Psi_{elec}(\mathbf{r}; \mathbf{R}) \quad (2.10)$$

The collection of all possible nuclear configurations, \mathbf{R} together with the associated energies, $E(\mathbf{R})$, defines a potential energy surface, $V(\mathbf{R})$ for the nuclei.

Now we can go back to the total Hamiltonian, and integrate over all the electron positions \mathbf{r} , ignoring any inconvenient term, to obtain an approximate Schrödinger equation for the nuclei:

$$\langle \Psi_{elec}(\mathbf{r}, \mathbf{R}) | \hat{H}_{tot} | \Psi_{elec}(\mathbf{r}, \mathbf{R}) \rangle \cong \hat{H}_{nucl} = \hat{T}_{nucl}(\mathbf{P}, \mathbf{R}) + V(\mathbf{R}) \quad (2.11)$$

with

$$(\hat{T}_{nucl}(\mathbf{P}, \mathbf{R}) + V(\mathbf{R})) \Psi_{nucl}(\mathbf{R}) = E_{nucl} \Psi_{nucl}(\mathbf{R}) \quad (2.12)$$

2.2.1 The nuclear Schrödinger equation

Both approximate Schrödinger equations (for electrons eq. 2.10 and for nuclei eq. 2.12) are still much too hard to solve exactly (they are partial differential equations in $3N$ particle coordinates), so we have to make more approximations.

$V(\mathbf{R})$ is usually expanded to second order \mathbf{R} about a stationary point \mathbf{R}_0 :

$$V(\mathbf{R}) \cong V(\mathbf{R}_0) + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right) (\mathbf{R}_i - \mathbf{R}_{0i})(\mathbf{R}_j - \mathbf{R}_{0j}) \quad (2.13)$$

and then the translations, rotations, and vibrations are each treated separately, neglecting any inconvenient terms that couple the different coordinates. In this famous "rigid-rotor-harmonic-oscillator (RRHO)" approximation, analytical formulas are known for the energy eigenvalues, and for the corresponding partition functions Q (look in any Phys.Chem. textbook).

This approximate approach has the important advantage that we do not need to solve the Schrödinger equation for the electrons at very many \mathbf{R} 's: we just need to find a stationary point \mathbf{R}_0 , and compute the energy and the second derivatives at that \mathbf{R}_0 . Many computer programs have been written that allow one to compute the first and second derivatives of $V(\mathbf{R})$ almost as quickly as you can compute V . For example, for a system with 10 atoms and $3 \times 10 = 30$ coordinates \mathbf{R}_I , it takes about half a minute on a PC to compute $V(\mathbf{R}_0)$ and only about 13 more minutes to compute the $30 \times 30 = 900$ second derivatives $\left(\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right)$. If you tried to do this naively by finite differences, it

would take about 15 hours to arrive at the same result (and it would probably be less accurate because of finite differencing numerical errors.) The analytical first derivatives are used to speed the search for the stationary point (e.g. the equilibrium geometry) \mathbf{R}_0 . Often the geometry and the second derivatives are calculated using certain approximations, but the final energy $V(\mathbf{R}_0)$ is computed more accurately (since thermodynamics data and reaction rates are most sensitive to errors in $V(\mathbf{R}_0)$, and even poor approximations often get geometry and frequencies close to correct).

Therefore, as long as a second-order Taylor expansion approximation for V is adequate we are in pretty good shape. Molecules and transition states with "large amplitude motions" (i.e. the Taylor expansion is not adequate) are much more problematic, dealing with them is an active research area. Fortunately, there are many systems where the conventional second-order V , RRHO approximation is accurate.

2.2.2 The electronic Schrödinger equation

The question is now how to compute the required potential $V(\mathbf{R})$ which acts on the nuclei at a given geometry \mathbf{R} . What we need to solve is 2.10,

$$\hat{H}_{elec}(\mathbf{p}, \mathbf{r}; \mathbf{R}) \Psi_{elec}(\mathbf{r}; \mathbf{R}) = V(\mathbf{R}) \Psi_{elec}(\mathbf{r}; \mathbf{R})$$

where in a vacuum, in the absence of fields, and neglecting magnetic effects

$$\hat{H}_{elec}(\mathbf{R}) = -\frac{1}{2} \sum_n \nabla_n^2 + \sum_{I < J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{In} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_n|} + \sum_{n < m} \frac{1}{|\mathbf{r}_m - \mathbf{r}_n|} \quad (2.14)$$

and because the electrons are indistinguishable fermions any permutation of two electrons must change the sign of the wavefunction $\Psi_{elect}(\mathbf{r}; \mathbf{R})$ (this is a really important constraint called the Pauli exclusion principle, it is the reason for the specific structure of the periodic table).

In addition, because the spin is a good quantum number we can chose the electronic wavefunction to be simultaneously an eigenfunction of the spin operator:

$$S^2 |\Psi_{elec}\rangle = S(S+1) |\Psi_{elec}\rangle \quad (2.15)$$

$$S_z |\Psi_{elec}\rangle = S_z |\Psi_{elec}\rangle \quad (2.16)$$

We can write Ψ_{elec} in a form that will guarantee it satisfies the Pauli principle, namely using the Slater determinant many-electron wavefunctions:

$$\Psi_{el}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{m_1, m_2, \dots, m_N} C_{m_1, m_2, \dots, m_N} |\phi_{m_1}(\mathbf{r}_1) \phi_{m_2}(\mathbf{r}_2) \dots \phi_{m_N}(\mathbf{r}_N)|$$

where

$$|\phi_{m_1}(\mathbf{r}_1) \phi_{m_2}(\mathbf{r}_2) \dots \phi_{m_N}(\mathbf{r}_N)| = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{m_1}(\mathbf{r}_1) & \phi_{m_2}(\mathbf{r}_1) & \dots & \phi_{m_N}(\mathbf{r}_1) \\ \phi_{m_1}(\mathbf{r}_2) & \phi_{m_2}(\mathbf{r}_2) & \dots & \phi_{m_N}(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{m_1}(\mathbf{r}_N) & \phi_{m_2}(\mathbf{r}_N) & \dots & \phi_{m_N}(\mathbf{r}_N) \end{vmatrix}$$

The components of the Slater determinant, $\phi_{m_i}(\mathbf{r}_i)$, are one-electron molecular orbitals which are usually given as an expansion in "atomic orbitals", χ_n :

$$\phi_m(\mathbf{r}, s) = \sum_n D_{mn} \chi_n(\mathbf{r}) \otimes s \quad (2.17)$$

(\mathbf{r} stays for the Cartesian coordinates (x, y, z) and s is the spin variable ($s \in \{\alpha, \beta\}$))

The collection of coefficients $D_{...}$ and $C_{...}$ fully characterizes the solution of the electronic Schrödinger equation for atoms and molecules.

The main subject of this course is a discussion of the approximation methods for the solution of the Schrödinger equation for the electrons (given by the coefficients $C_{...}$ and $D_{...}$), which provides the potential for the nuclei dynamics $V(\mathbf{R})$. IF time allows, towards the end of the course, we will discuss some of the semiclassical adiabatic approaches for the nuclear dynamics such as the Car-Parrinello method and QM/MM molecular dynamics.

Before starting, we have however to translate this problem into a formulation suited for computation. Using appropriate basis function it is possible to translate 2.10 into a simple linear algebra problem, which can be solved using efficient computer software (see for instance the parallel package for the solution of linear algebra problem LAPACK: Linear Algebra PACKage (www.netlib.org/lapack)²).

2.3 Basis sets, linear algebra and the secular equation

2.3.1 Basis kets and matrix representation

Given an Hermitian operator A , its eigenkets (eigenfunctions), $|\varphi_a\rangle$ form a complete orthonormal set. An arbitrary ket, $|\alpha\rangle$ can be expanded in terms of the eigenkets of A .

$$|\alpha\rangle = \sum_a c_a |\varphi_a\rangle \quad (2.18)$$

Multiplying with $\langle\varphi_{a'}|$ on the left and using the orthogonality property $\langle\varphi_{a'}|\varphi_a\rangle$, we can immediately find the coefficient,

$$c_a = \langle\varphi_a|\alpha\rangle \quad (2.19)$$

In other words, we have

$$|\alpha\rangle = \sum_{a'} |\varphi_{a'}\rangle \langle\varphi_{a'}|\alpha\rangle, \quad (2.20)$$

²LAPACK is written in Fortran90 and provides routines for solving systems of simultaneous linear equations, least-squares solutions of linear systems of equations, eigenvalue problems, and singular value problems. The associated matrix factorizations (LU, Cholesky, QR, SVD, Schur, generalized Schur) are also provided, as are related computations such as reordering of the Schur factorizations and estimating condition numbers. Dense and banded matrices are handled, but not general sparse matrices. In all areas, similar functionality is provided for real and complex matrices, in both single and double precision.

LAPACK routines are written so that as much as possible of the computation is performed by calls to the Basic Linear Algebra Subprograms (BLAS). LAPACK was designed at the outset to exploit Level 3 BLAS – a set of specifications for Fortran subprograms that do various types of matrix multiplication and the solution of triangular systems with multiple right-hand sides. Because of the coarse granularity of the Level 3 BLAS operations, their use promotes high efficiency on many high-performance computers, particularly if specially coded implementations are provided by the manufacturer.

Highly efficient machine-specific implementations of the BLAS are available for many modern high-performance computers. For details of known vendor- or ISV-provided BLAS, consult the BLAS FAQ. Alternatively, the user can download ATLAS to automatically generate an optimized BLAS library for the architecture. A Fortran77 reference implementation of the BLAS is available from netlib; however, its use is discouraged as it will not perform as well as a specially tuned implementations.

which is analogous to an expansion of a vector \vec{v} in the (real) Euclidean space:

$$\vec{v} = \sum_i \hat{e}_i (\hat{e}_i \cdot \vec{v}), \quad (2.21)$$

where $\{\hat{e}_i\}$ form an orthogonal set of unit vectors.

An important operator is the projection operator Λ_a , which acting on a ket state $|\alpha\rangle$ gives the component of the ket parallel to $|\varphi_a\rangle$,

$$(|\varphi_a\rangle\langle\varphi_a|)|\alpha\rangle = |\varphi_a\rangle\langle\varphi_a|\alpha\rangle = c_a|\varphi_a\rangle. \quad (2.22)$$

Since the sum of all projections of a ket $|\alpha\rangle$ gives back the same ket,

$$\sum_a |\varphi_a\rangle\langle\varphi_a| = 1 \quad (2.23)$$

where 1 is the identity operator. This representation of the unity operator is called the **completeness relation**.

Having specified the base ket, we now show how to represent an operator X , by a square matrix. Using the completeness relation twice, we can write the operator X as

$$X = \sum_{a'} \sum_a |\varphi_{a'}\rangle\langle\varphi_{a'}|X|\varphi_a\rangle\langle\varphi_a| \quad (2.24)$$

There are altogether N^2 numbers of the form $\langle\varphi_{a'}|X|\varphi_a\rangle$, where N is the dimensionality of the ket space. We may arrange them into a $N \times N$ square matrix where the column and row indices appear as

$$X \doteq \begin{pmatrix} \langle\varphi_1|X|\varphi_1\rangle & \langle\varphi_1|X|\varphi_2\rangle & \dots \\ \langle\varphi_2|X|\varphi_1\rangle & \langle\varphi_2|X|\varphi_2\rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (2.25)$$

where the symbol \doteq stands for "is represented by".

Knowing all (infinite many) matrix elements $\langle\varphi_{a'}|X|\varphi_a\rangle$ of the operator X is equivalent to the knowledge of the operator itself (in the same way as knowing the 3 components of a vector in the Euclidean space is sufficient to determine its orientation and length).

In the same way we describe operators by matrices, kets can be described by column vectors,

$$|\alpha\rangle \doteq \begin{pmatrix} \langle\varphi_1|\alpha\rangle \\ \langle\varphi_2|\alpha\rangle \\ \langle\varphi_3|\alpha\rangle \\ \vdots \end{pmatrix} \quad (2.26)$$

and bras as row vectors,

$$\begin{aligned} \langle \beta | &\doteq (\langle \beta | \varphi_1 \rangle \quad \langle \beta | \varphi_2 \rangle \quad \langle \beta | \varphi_3 \rangle \quad \cdots) = \\ &= (\langle \varphi_1 | \beta \rangle^* \quad \langle \varphi_2 | \beta \rangle^* \quad \langle \varphi_3 | \beta \rangle^* \quad \cdots) . \end{aligned} \quad (2.27)$$

Therefore, the action of an operator on a ket can be represented as a matrix multiplication with a vector (link to your linear algebra course).

2.3.2 Basis functions in quantum chemistry

In one of the most frequent approximations used in quantum chemistry, the complex one-electron or even many-electron molecular wavefunctions are described in basis of atom centered functions. These simplified atomic orbitals are often taken to have the form of sums of Gaussians centered on the atoms times a polynomial, P_l , in the electron coordinates relative to that atom:

$$\chi_n(\mathbf{r}) = \sum_l N_l^n \exp(-\alpha_l^n (|\mathbf{r} - \mathbf{R}_l^n|^2)) P_l(\mathbf{r} - \mathbf{R}_l^n) \quad . \quad (2.28)$$

There are conventional sets of these atomic orbitals that are used, that cover the polynomials up to a certain order with certain choices of " α "; these are called "basis sets" and are given names like "6-31G*", "TZ2P", and "cc-pVQZ". The general procedure is to pick one of these basis sets, and then to vary the C 's and the D 's in

$$\begin{aligned} \Psi_{el}(\mathbf{r}_1, s_1, \mathbf{r}_2, \dots, \mathbf{r}_N, s_N) &= \\ &= \sum_{m_1, m_2, \dots, m_N} C_{m_1, m_2, \dots, m_N} |\phi_{m_1}(\mathbf{r}_1, s_1) \phi_{m_2}(\mathbf{r}_2, s_2) \cdots \phi_{m_N}(\mathbf{r}_N, s_N)| \end{aligned} \quad (2.29)$$

with

$$\phi_m(\mathbf{r}, s) = \sum_n D_{mn} \chi_n(\mathbf{r}) \otimes s \quad (2.30)$$

to try to find an approximate Ψ_{elec} that solves the Schrödinger equation as closely as possible. If your basis set has a very good overlap with the true wavefunction, you will be able to achieve good accuracy only varying a few C 's and D 's.³

2.3.3 The variational principle and the secular equation

The variational problem consists in varying the C 's and D 's to minimize

$$E[\Psi_{elec}] = E(C \dots, D \dots) = \frac{\langle \Psi_{elec} | \hat{H}_{elec} | \Psi_{elec} \rangle}{\langle \Psi_{elec} | \Psi_{elec} \rangle} \quad (2.31)$$

³More about the specific basis functions used in computational quantum chemistry will follow in Chapter 3.

For any trial wavefunction, Ψ_{elec}^{trial} , the following inequality holds

$$E[\Psi_{elec}] \leq \frac{\langle \Psi_{elec}^{trial} | \hat{H}_{elec} | \Psi_{elec}^{trial} \rangle}{\langle \Psi_{elec}^{trial} | \Psi_{elec}^{trial} \rangle} . \quad (2.32)$$

This is called the variational principle. The evaluation of the integral requires $\mathcal{O}(N_{\text{basis}}^3)$ operations. (Gaussian functions are used because they allow the integrals to be computed analytically.) Typically a basis set might include 15 atomic orbitals for each atom (except H atoms which do not need so many) and you would vary the $(15 * N_{\text{atoms}})^2$ coefficients D_{mn} . The number of possible coefficients C is much larger, something like N_{basis} raised to the $N_{\text{electrons}}$ power, so it is almost always impossible to do anything with a complete expansion. Often people don't bother to vary the C 's, or only allow a small fraction of the C 's to vary independently, to reduce the number of parameters. By allowing the C 's to vary, you are allowing to account for the fact that the different electrons are correlated with each other: when one is close to the nucleus the others are likely to be far away.

2.3.4 Linear variational calculus

In variational calculus, stationary states of the energy functional are found within a subspace of the Hilbert space. An important example is **linear variational calculus**, in which the subspace is spanned by a set of basis vectors $|\Xi_m\rangle, m = 1, \dots, M$, that we take to be orthonormal. Here we consider the case of fixed atomic orbital expansion coefficients (D_{\dots}) and to-be-optimized Slater expansion coefficients (C_{\dots}) (for example a set of M Slater determinants, $|\Xi_m\rangle = |\phi_{m_1}(\mathbf{r}_1)\phi_{m_2}(\mathbf{r}_2)\dots\phi_{m_N}(\mathbf{r}_N)|$). For a state

$$\begin{aligned} \Psi_{el}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \sum_{m_1, m_2, \dots, m_N} C_{m_1, m_2, \dots, m_N} |\phi_{m_1}(\mathbf{r}_1)\phi_{m_2}(\mathbf{r}_2)\dots\phi_{m_N}(\mathbf{r}_N)| \\ &\doteq \sum_{m=1}^M c_m |\Xi_m\rangle \end{aligned} \quad (2.33)$$

the energy functional is given by

$$E = \frac{\sum_{p,q=1}^M c_p^* c_q H_{p,q}}{\sum_{p,q=1}^M c_p^* c_q \delta_{p,q}} \quad (2.34)$$

with

$$H_{p,q} = \langle \Xi_p | \hat{H}_{elec} | \Xi_q \rangle \quad (2.35)$$

The **stationary states** follow from the condition that the derivative of this functional with respect to the c_p vanishes, which leads to

$$\sum_{q=1}^M (H_{p,q} - E \delta_{p,q}) c_q = 0, \quad \text{for } p = 1, \dots, M. \quad (2.36)$$

Equation (2.36) is an eigenvalue problem which can be written in the matrix notation

$$\mathbf{H} \mathbf{C} = E \mathbf{C} \quad (2.37)$$

This is the Schrödinger equation formulated for a finite, orthonormal basis. Although in principle it is possible to use nonlinear parameterizations of the wave function, linear parameterizations are used in the large majority of cases because of the simplicity of the resulting method, allowing for numerical matrix diagonalization techniques. **The lowest eigenvalue of (2.37) is always higher than or equal to the exact ground state energy, as the ground state is the minimal value assumed by the energy functional in the full Hilbert space.** If we restrict ourselves to a part of this space, then the minimum value of the energy functional must always be higher than or equal to the ground state of the full Hilbert space. Including more basis functions into our set, the subspace becomes larger, and consequently the minimum of the energy functional will decrease (or stay the same). For the specific case of linear variational calculus, this result can be generalized to higher stationary states: they are always higher than the equivalent solution to the full problem, but approximate the latter better with increasing basis set size.

Because the computer time needed for matrix diagonalization scales with the third power of the linear matrix size (it is called a $\mathcal{O}(M^3)$ process), the basis should be kept as small as possible. Therefore, it must be chosen carefully: it should be possible to approximate the solutions to the full problem with a small number of basis functions⁴.

In the case in which the basis consists of **nonorthonormal basis functions**, as is often the case in practical calculations, we must reformulate (2.37), taking care of the fact that the *overlap matrix* \mathbf{S} , whose elements S_{pq} are given by

$$S_{p,q} = \langle \Xi_p | \Xi_q \rangle \quad (2.38)$$

is not the unit matrix. This means that in Eq. (2.34) the matrix elements δ_{pq} of the unit matrix, occurring in the denominator, have to be replaced by S_{pq} , and we obtain (for the derivation see the next section)

$$\mathbf{H} \mathbf{C} = E \mathbf{S} \mathbf{C}. \quad (2.39)$$

This looks like an ordinary eigenvalue equation, the only difference being the matrix \mathbf{S} in the right hand side. It is called a generalized eigenvalue equation and there exist computer programs for solving such a problem.

⁴The fact that the basis in (continuous) variational calculus can be chosen so much smaller than the number of grid points in a finite difference approach implies that even though the latter can be solved using special $\mathcal{O}(N)$ methods for sparse systems, they are still far less efficient than variational methods with continuous basis functions in most cases. This is the reason why, in most electronic structure calculations, variational calculus with continuous basis functions is used to solve the Schrödinger equation.

2.4 Overview of possible approximate solutions of the electronic Schrödinger equation

The most commonly used approximate methods for the solution of the electronic molecular Schrödinger equation are:

- **Semi-empirical** (MNDO, AM1, PM3, etc.): use a single Slater determinant (only one C is equal 1 while all the others are set to 0). Vary the coefficients D, but just use empirical estimates rather than the true integrals. *Very cheap, but only accurate for molecule similar to those used to develop the empirical estimates.*

- **DFT** (B3LYP, BLYP, PW91, etc.): slightly empirical, but much more reliable than semi-empirical methods. CPU: cheap, same as HF $\mathcal{O}(N^3)$. Errors ~ 4 kcal/mole (comparable accuracy to MP2 but much cheaper). Preferred method for geometries, second derivatives, transition-metal containing systems.

- **HF** (Hartree-Fock, SCF): only one many-electrons Slater determinant is used. Vary the D's. All terms calculated 'ab-initio' within the mean field approximation, no empirical parameters. *CPU: cheap $\mathcal{O}(N^3)$ errors ~ 15 kcal/mol.*

- **MP2, MP4** (Moller-Plesset, MBPT): Vary the D's first, then set the C's to the values given by perturbation theory (you don't freely vary these C's, saving CPU). *MP2: medium CPU: $\mathcal{O}(N^5)$, errors ~ 5 kcal/mol.*

- **CI, CISD, QCISD** (Configuration Interaction): Vary the coefficients D first, freeze them, then vary a lot of the coefficients C. *Expensive. Not used much anymore, CCSD is preferred.*

- **MCSCF, CASSCF**: vary a finite set of C's and all the D's simultaneously. *Expensive. Good for understanding cases where several electronic states have comparable energies. User expertise required to select which C's to vary.*

- **CAS-PT2**: Determine the D's and some C's by CASSCF, then determine more C's by perturbation theory. *Not much more expensive than CASSCF. Sometimes very good, but not reliable.*

- **MRCI** (multi reference CI): Determine the D's and some C's by CASSCF or MCSCF, freeze these, then allow many of the C's to vary. *Super expensive. Very high accuracy for small systems.*

- **CCSD, CCSD(T)** (Coupled Cluster): Vary the D's, fix them, then vary a lot of the C's, but constraining certain relationships between the C's.

This allows you to effectively use a longer expansion without increasing the number of adjustable parameters so much. The constraints force the solution to be "size-consistent", i.e. two molecules calculated simultaneously have exactly the same energy as two molecules calculated separately.

Expensive. Often very accurate.

- **Extrapolations** ("Composite Methods"): G2, G3, CBS-q, CBS-Q, CBS-QB3, CBS-RAD Run a series of the above calculations with different size basis sets, following some recipe. The results from all these calculations are extrapolated to an estimate of the true potential $V(R)$. These methods give excellent accuracy in less CPU time than CCSD or MRCI. However, the multiple steps involved provide many opportunities for something to go wrong. *Accuracy: usually 1-2 kcal/mol.*

Some Practical Warnings

- 1) The optimization (SCF/HF/DFT/CASSCF/MRSCF) problem required to solve for the D 's is nonlinear and has multiple solutions, only one of which is the one you want (usually you want the lowest energy solution). So you may end up converging to a wavefunction which is qualitatively incorrect, perhaps it corresponds to an electronically excited state.
- 2) Most of the quantum chemistry methods have problems (convergence, accuracy) with systems where there are low-lying electronic states (close to the ground state). In these cases, sometimes the numbers computed are completely nuts, other times they are subtly wrong. This is particularly a problem for transition states and where there are several lone pair electrons in the system. If you must study these systems, get expert assistance.
- 3) Many molecules have multiple geometrical conformations (local minima in $V(\mathbf{R})$), and sometimes there are multiple saddle points that might be confused with the transition state (TS). Look at your structures, if they are not what you expected, investigate. Also, it is worth some effort to make sure your initial guess at the molecular geometry is quite good, otherwise the geometry-optimization algorithm may get lost and waste a lot of CPU time to no avail. If you are having troubles, you can constrain some of the coordinates to make things easier for the optimizer.
- 4) For radicals and other open-shell systems, compare your computed solutions $\langle S^2 \rangle$ with the theoretical value $S(S + 1)$. If your number is way off, chances are you have other problems as well. Sometimes you can use "restricted" methods like ROHF and RMP2, or spin-projection methods to fix this "spin-contamination" problem.
- 5) Every method runs into problems sometimes, and sometimes they are quite subtle. It is a good idea to double check your calculation with another calculation done using a very different method. If they both agree you can be pretty confident that your result is real.