École polytechnique fédérale de Lausanne

Introduction to Electronic Structure Methods

Exercises

Assistants:
Mathias DANKL (mathias.dankl@epfl.ch, BCH 4110)
François MOUVET (francois.mouvet@epfl.ch, BCH 4111)
Justin VILLARD (justin.villard@epfl.ch, BCH 4111)

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Computational chemistry is a powerful tool for the prediction and validation of molecular properties. During the following exercise sessions, you will apply the techniques that have been treated in the lecture to both theoretical and practical problems. Although the scope of this course is too small to give a complete overview of what can be done using computational chemistry (and we note that we can do a lot), you should be able to gain some insight into the way computational problems can be tackled. In the applied problem sessions, you will learn how to calculate various molecular properties using different approaches. You will use a widespread and powerful computer code, *Gaussian 09*, as well as the visualisation software MOLDEN and the operating system Linux.

Acknowledgements

The script accompanying the excercises was completely rewritten and restructured by Martin P. Bircher and Siri C. van Keulen. It was inspired by a first version by Dr. Manuel Dömer and Dr. Elizabeth Brunk, which was loosely based on the script "Introduction to the Gaussian Quantum Chemical Code" by Dr. Samuel Arey and Dr. Geoffrey Wood.

Grading and attendance

Please note that your attendance to the exercises is *mandatory*, during the entire 2 hours of the sessions. All the exercises can be finished within these 2 hours, and the assistants will be with you to answer any questions that you may have. Every set of excercises will be accompanied by a written report that can be handwritten or typed in any format you like (Word, Latex, ...).
During all, except for the first exercise session, each person will spend 5-10 minutes with an assistant where they will be asked questions about the past week's exercises and the respective report, which must have been handed in as a hard copy at the beginning of the session. The answers to these questions will be graded and contribute 1/3 to your overall grade. The worst report will not count in the grade for the exercises. Please note that the first session on linear algebra is an exception, as the grading will be based on the written report only. Reports need to be handed in one week after the respective session if no other indication from the assistants.

Contents

This list gives an overview of the topics we will be covering during the next week.

- Linear Algebra in Quantum Mechanics I

- Linear Algebra in Quantum Mechanics II
  Review: Bra-Ket Notation and Eigenbases in Hilbert Space

- The Hydrogen Atom: Hartree-Fock Calculations in Gaussian09

- Large Basis Sets, Dissociation Energy and Geometry Optimisation

- Post Hartree-Fock Methods: MPn and Configuration Interaction

- Troubleshooting in Gaussian09 - Density Functional Theory I

- Solutions to the Written Exam
  Review: Basic Concepts of Kohn-Sham DFT

- Density Functional Theory II - Comparison with (Post) Hartree-Fock Methods

- Potential Energy Scans and Visualisation of Trajectories

- Finding Transition States and Barrier Heights: First Order Saddle Points

- Finding Transition States and Barrier Heights: Intrinsic Reaction Coordinates (IRC)

- Question Hour before Oral Exam

Questions

We are here to help - please do not hesitate to contact us outside the scheduled hours. You may contact us by mail or schedule an appointment to discuss with us in person; just stop by our offices.
If you notice any typos or mistakes in the exercise script, please do let us know.

1 Linear Algebra in Quantum Mechanics

1.1 Basic Linear Algebra

This chapter summarises concepts that you are familiar with from your linear algebra and quantum mechanics courses and that are the most relevant to computational chemistry. It is meant as a review rather than an introduction. The first paragraphs deal with the fundamental concepts, and practical examples in quantum mechanics shall be given towards the end of the chapter along with a set of exercises. (For those interested, some additional information is given in parentheses; you may find this useful if you ever wish to go through the literature.)

Operators

In classical mechanics, an observable is described by a function. Instead, in quantum mechanics, an observable is represented by a linear operator that acts on a wavefunction. An operator is itself a function that, when applied to the state of a system, returns another function. A simplified view would describe it as an instruction to carry out some *operation* on a function to obtain the desired result - this may be anything ranging from a simple multiplication to differentiation, integration etc. (Strictly speaking, the linear operators used in quantum mechanics are special cases of a linear mapping $V \to W$ where $V = W$ - linear algebra plays a crucial role in quantum mechanics.)

Eigenfunctions and eigenvalues

Applying an operator $\hat{A}$ to some function f can result in the function being changed, but it may also result in the operator returning the same function, multiplied by a scalar:

$$\hat{A}f = \lambda f. \tag{1}$$

The multiplicative constant λ is the *eigenvalue* of the equation, and the function f is referred to as the *eigenfunction* of the operator $\hat{A}$. These terms are derived from the German word "eigen", meaning "its own", *i.e.* an eigenfunction of an operator is implied to belong to said operator. (We note *en passant* that the set of eigenvalues of an operator is called its *spectrum*.)

Together, the eigenfunctions form a *complete basis* such that any general function g may be expressed in terms of a linear combination of the eigenfunctions:

$$\hat{A}f_i = \lambda_i f_i \tag{2}$$

$$g = \sum_i c_i f_i, \tag{3}$$

with c_i being the expansion coefficient and the sum running over all f_i. The effect of an operator on an arbitrary function g can thus be expressed by decomposing g in terms of

its *basis functions*:

$$\hat{A}g = \hat{A} \sum_i c_i f_i = \sum_i c_i \hat{A} f_i = \sum_i c_i \lambda_i f_i. \qquad (4)$$

A quite comprehensive list of quantum mechanical operators can be found at the end of this chapter.

Applying several operators: Commutators

For some operators such as simple multiplications, the order in which the operators are applied to the function does not matter. Consider this (trivial) example:

$$x \cdot y \cdot f(x) = y \cdot x \cdot f(x). \qquad (5)$$

Turning to derivatives, however, this is not the case anymore:

$$x \cdot \frac{\partial}{\partial x} f(x) \neq \frac{\partial}{\partial x} x \cdot f(x). \qquad (6)$$

It is trivial to see that it is indeed relevant in which order operators are applied to a function. We therefore define the commutator of two operators as:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}. \qquad (7)$$

Two operators $\hat{A}, \hat{B}$ are said to *commute* if $\left[\hat{A}, \hat{B}\right] = 0$; if they commute, the order in which they are applied to a function does not matter - if they do not, i.e. if the commutator is nonzero, it does matter. Note that the commutator plays a crucial role in quantum mechanics, as it determines whether two observables can be simultaneously determined (*cf.* the Heisenberg uncertainty principle). Commuting operators share the same eigenfunctions (or, *vice versa*, operators sharing the same eigenfunctions will commute).

1.2 Linear Algebra and Quantum Mechanics: Hermiticity and Matrix Representations

From here on, operators will be applied to some (wave)function ϕ, ψ rather than an arbitrary function f. This is just a matter of notation and goes, of course, without loss of generality. (Note that we chose not to write $\phi(x)$ or the like, because it is not relevant whether we use the position or the momentum wavefunction, *cf.* the bra-ket notation that will be discussed below.)

Hilbert Space and Bra-Ket Notation

Recalling that any arbitrary function can be expressed as a weighted superposition of eigenfunctions of their underlying operator, one needs to define a mathematical *functional space* in which these eigenfunctions reside. An N-dimensional *euclidian space* is restricted

to real numbers, but the eigenfunctions we are interested in may as well be complex valued.[1]

The concept of euclidian space was generalised by Hilbert onto an infinite dimensional complex space of square integrable functions, the *Hilbert space*. (A Hilbert space is a *Banach space*; a vector space that has a well-defined metric such that the distance between two vectors as well as the magnitude of a vector can be computed.)

Each instantaneous state is described by a unit vector or a *state vector* in Hilbert space. Just like a position vector in cartesian space, the state vector is expressed in terms of the orthogonal basis vectors that are formed by all the eigenfunctions. (The chapter on Hermitian operators will justify this. One should also note that 'all eigenfunctions' refers to all eigenfunctions of an operator to which the Hilbert space under consideration is associated.) All these eigenfunctions taken together encode all the relevant information: Being a complete set (a *basis*), they are all that is needed to describe any arbitrary function g (*cf.* preceeding chapter).

A proper notation that accurately describes vectors with an infinite (but countable) number of elements - such as those in Hilbert space - was introduced by Paul Dirac. In *bra-ket (or Dirac) notation*, a vector in Hilbert space is denoted by a *ket*

$$|\Psi\rangle = \begin{pmatrix} \vdots \end{pmatrix}, \tag{8}$$

which is a column vector. In one-to-one correspondence to the space formed by the kets, there exists a dual space consisting of *bra* vectors:

$$\langle\Psi| = (\cdots), \tag{9}$$

which is the adjoint of the ket (*i.e.* a row vector that is the complex conjugate of the ket). As both bra and ket are unit vectors, their norm is 1. In Hilbert space, an inner product of two vectors $\langle\Phi,\Psi\rangle$ is always defined. For $\Phi = \Psi$, the inner product defines the norm of the vectors - we will leave further specification as an exercise question. For two orthogonal basis vectors ψ_i, ψ_j, we have that:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}, \tag{10}$$

where δ_{ij} denotes the Kronecker delta. Note that bras and kets themselves are not specified as being dependent on position or momentum, simply because the position and momentum wavefunctions are obtained by *projecting* their representation out of a ket in Hilbert space, as will be shown later. (However, time dependence of a state is often implicit.)

Applying bra-ket notation to the previously discussed description of any function in terms of eigenfunctions, any state of the system is given as a linear combination:

$$|\Psi\rangle = \sum_{j}^{\infty} c_j |\psi_j\rangle, \tag{11}$$

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[1]Cartesian space is just an example of a 3-dimensional euclidian space.

where we introduced capital greek letters for the state of the system, and lower case letters for its basis (its eigenfunctions.) The expansion coefficients are simply the projections of the basis ψ_j onto the total state function Ψ (thinking of cartesian vectors, the projection of the x axis out of some vector yields the length of the vector on the x axis - the concept for a wavefunction expansion is the same).

$$c_j = \langle \psi_j | \Psi \rangle \tag{12}$$

Because every state is normalised, just like the basis vectors it is built upon, any state Ψ must also be of the same norm. This requirement is conserved if and only if the normalisation $\sum_j c_j^2 = 1$ is imposed.

Valid Quantum Mechanical Operators: Linearity and Hermiticity

In order for an operator to be a valid quantum mechanical operator, it must be *linear*

$$\hat{A}(\psi + \phi) = \hat{A}\psi + \hat{A}\phi. \tag{13}$$

For operators that describe a state that is physically observable, it is further required that the operator be *Hermitian*. (In the strict mathematical sense, this requirement implies linearity, but physicists use the less specific definition of hermiticity as given below.) A Hermitian operator is defined as an operator that is equal to its conjugate transpose:

$$\hat{A}^T = \overline{\hat{A}}. \tag{14}$$

(Strictly speaking, this is true for an operator in a finite vector space V; a Hermitian operator being a special case of a self-adjoint operator. Hermitian operators are normal operators, whence the spectral theorem holds.) The eigenvalues of a Hermitian operator have some useful properties; they are *real* (which is a direct consequence of the definition of a Hermitian operator, as it shall be pointed out later again) and *orthogonal* to each other (this is why basis vectors in Hilbert space are orthogonal - and this is what allows for algebraic transformations in euclidian space to be easily extended onto the complex Hilbert space).

Matrix Representation of Operators

The definition of a Hermitian operator being based on properties known from matrices implies a link between the two. Indeed, any operator can be written in a matrix form.

Consider another system Φ that is defined analogously to Ψ:

$$|\Psi\rangle = \sum_j^\infty c_j |\psi_i\rangle \quad ; \quad |\Phi\rangle = \sum_k^\infty d_k |\psi_k\rangle, \tag{15}$$

and an operator such that

$$|\Phi\rangle = \hat{A} |\Psi\rangle. \tag{16}$$

(Since a Hermitian operator is a linear map $V \to V$, the basis remains unchanged, but the expansion coefficients differ.) The *matrix elements* of the operator $\hat{A}$ in the basis $\{\psi\}$ are now given as

$$A_{ij} = \langle \psi_i | \hat{A} | \psi_j \rangle, \tag{17}$$

describing how the operator acts between the orthogonal basis vectors ϕ_i and ϕ_j.

From the above, we deduce that

$$\sum_k^\infty d_k | \psi_k \rangle = \hat{A} \sum_j^\infty c_j | \psi_j \rangle, \tag{18}$$

and after multiplication by $\sum_i^\infty \langle \psi_i |$, exploiting orthogonality of the basis and applying the above definition of the operator's matrix elements, it follows that:

$$d_i = \sum_j A_{ij} c_j, \tag{19}$$

where the summation over an infinite but countable number of elements is implicitly assumed. This equation can be rewritten in matrix form:

$$\begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_i \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1j} \\ A_{21} & A_{22} & \cdots & A_{2j} \\ \vdots & \vdots & \ddots & \vdots \\ A_{i1} & A_{i2} & \cdots & A_{ij} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_j \end{pmatrix}, \tag{20}$$

c, d are vectors of expansion coefficients of Φ, Ψ respectively. Operators for which $A_{ij} = 0$ are, just like their underlying matrix, *diagonal*.

1.3 The Wavefunction and its Properties - Projections out of Hilbert Space

So far, any state Ψ was discussed as an abstract unit vector in Hilbert space that is expanded over a basis of eigenfunctions. In this chapter, it will be demonstrated how the familiar picture of a wavefunction in position representation is extracted from Hilbert space and what properties such a wavefunction has. The theory outlined so far will be applied to the energy eigenvalue problem of Schrödinger (the time-independent Schrödinger equation).

The Wavefunction in Position Representation

The more abstract bra-ket notation and the notation of the wavefunction as being position or momentum dependent are often used interchangeably. Position and momentum wavefunctions are obtained by *projecting* the state function in Hilbert space onto position or momentum space using the respective operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. First, we note that the

(non-square integrable) real space basis at a point $\mathbf{r}_0$ is given by a delta function, which is the eigenfunction of the real space operator $\hat{\mathbf{r}}_0$:

$$\xi_{\mathbf{r}_0}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{21}$$

In bra-ket notation, we shall denote this basis function $|\mathbf{r}_0\rangle$. The corresponding *projection operator* $\hat{P}$ is given by:

$$\hat{P}_{\mathbf{r}_0} = |\mathbf{r}_0\rangle \langle \mathbf{r}_0|, \tag{22}$$

with the closing relation:

$$\int |\mathbf{r}_0\rangle \langle \mathbf{r}_0| \, \mathrm{d}\mathbf{r}_0 = \mathbb{1}, \tag{23}$$

where $\mathbb{1}$ is a unit matrix. Applying the projection operator onto the wavefunction, one has

$$|\psi\rangle = \int |\mathbf{r}_0\rangle \langle \mathbf{r}_0|\Psi\rangle \, \mathrm{d}\mathbf{r}. \tag{24}$$

The representation in the momentum basis can be developed analogously. The inner product $\langle \mathbf{r}_0|\Psi\rangle$ can be interpreted as the coefficient of the expansion of $|\Psi\rangle$ on the basis $|\mathbf{r}_0\rangle$. After multiplication by a suitably chosen ket and making use of the orthogonality of the basis, one then readily finds:

$$\Psi(\mathbf{r}, t) = \langle \mathbf{r}|\Psi\rangle \tag{25}$$
$$\Psi(\mathbf{p}, t) = \langle \mathbf{p}|\Psi\rangle, \tag{26}$$

where the position and momentum vectors $\mathbf{r}$ and $\mathbf{p}$ are 3-dimensional. (Often, $\mathbf{r}$ is just used for the length of a vector in position representation, and $\mathbf{q}$ is used for coordinates. We will however resort to using $\mathbf{r}$ throughout this script to denote a vector of (cartesian) coordinates.) Position and momentum wavefunction still contain all the information we need, and they conserve the properties of unit vectors in Hilbert space as discussed in the preceeding sections. Specifically, the L^2 norm in real space is naturally given by:

$$\langle \Psi|\Psi\rangle = \int \Psi^*(\mathbf{r}, t) \, \Psi(\mathbf{r}, t) \, \mathrm{d}\mathbf{r}. \tag{27}$$

Properties of Wavefunctions: The Example of Real Space

■ $\Psi(\mathbf{r}, t)$ is a real or complex, square integrable function such that

$$\Psi\left(\mathbf{r}, t\right)^* \Psi\left(\mathbf{r}, t\right) \quad = \quad \left|\Psi\left(\mathbf{r}, t\right)\right|^2 \quad \geq 0 \tag{28}$$

is always real.

■ $\Psi(\mathbf{r}, t)$ is a continuous function of its independent variables, and so are its first derivatives. Second derivatives may be discontinuous, but finite. (This is true for a finite potential, for an infinite potential, the first derivative may become discontinuous, such as at nuclear cusps.)

■ $\Psi(\mathbf{r}, t)$ has to be square integrable to be normaliseable (*cf.* definition of Hilbert space):

$$\int \Psi^*\left(\mathbf{r}, t\right) \Psi\left(\mathbf{r}, t\right) \mathrm{d}\mathbf{r} = 1. \tag{29}$$

■ $\Psi(\mathbf{r}, t)$ is defined up to a complex phase factor $e^{i\phi}$ of norm 1. This implies that $\Psi(\mathbf{r}, t)$ and $-\Psi(\mathbf{r}, t)$ describe the same state.

Probabilities and Observables

Whereas a wavefunction contains all the neccessary information, it lacks any direct physical interpretation. Its square, however, fulfills the requirements of a *probability distribution*. Namely, for a many-electron wavefunction, where N electrons are associated to N coordinate vectors $\{\mathbf{r}_i\}$:

$$P\left(\mathbf{r}_1, \mathrm{d}\mathbf{r}_1; \ldots; \mathbf{r}_N, \mathrm{d}\mathbf{r}_N\right) = \left|\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right)\right|^2 \mathrm{d}\mathbf{r} = \left|\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right)\right|^2 \mathrm{d}\mathbf{r}_1, \mathrm{d}\mathbf{r}_2, \ldots, \mathbf{d}\mathbf{r}_N. \tag{30}$$

The square of the wavefunction corresponds to the probability of finding all N electrons simultaneously in the infinitesimal volume elements $\mathrm{d}\mathbf{r}_1, \mathrm{d}\mathbf{r}_2, \ldots, \mathrm{d}\mathbf{r}_N$. The probability of finding electron 1 in $\mathrm{d}\mathbf{r}_1$ and all the other electrons anywhere else is given by the N-1 dimensional integral:

$$P\left(\mathbf{r}_1, \mathrm{d}\mathbf{r}_1\right) = \mathrm{d}\mathbf{r}_1 \int \cdots \int \Psi^*\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right) \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right) \mathrm{d}\mathbf{r}_2, \ldots, \mathrm{d}\mathbf{r}_N \tag{31}$$

Similarly, $P\left(\mathbf{r}_1, \mathrm{d}\mathbf{r}_1; \mathbf{r}_2, \mathrm{d}\mathbf{r}_2\right)$ will be given by a N-2 dimensional integral.

All physically measurable quantities, the *observables*, are associated to a corresponding

Hermitian operator $\hat{O}$ (it is common to denote operators that correspond to an observable by the letter O). Applying this operator to the state function of a system returns its eigenvalue if the state function is an eigenfunction of the operator; for a generic function Ψ, each eigenvalue of the underlying basis $\{\psi\}$ may be obtained, with a probability depending on the expansion coefficient c_i of the eigenfunction. The mean or *expectation value* of an observable O is then given by:

$$\left\langle \hat{O} \right\rangle = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \Psi | \hat{O} | \Psi \rangle \tag{32}$$

because of the normalisation condition.

Operators in Position Representation

- Position:

$$\hat{x} = x \cdot \quad ; \quad \hat{\mathbf{r}} = \mathbf{r} \tag{33}$$

- Momentum:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad ; \quad \hat{\mathbf{p}} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = -i\hbar \nabla \tag{34}$$

- Energy:

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \tag{35}$$

- Time:

$$\hat{t} = t \cdot \tag{36}$$

From the properties of a Hermitian operator, we have that

$$\int \Phi^* (\mathbf{r}) \hat{O} \Psi (\mathbf{r}) \, d\mathbf{r} = \left(\int \Psi^* (\mathbf{r}) \hat{O} \Phi (\mathbf{r}) \, d\mathbf{r} \right)^* \tag{37}$$

which proves that its eigenvalues are real, as stated earlier. This is a requirement for a physical observable and demonstrates why Hermitian operators are of great value in quantum mechanics.

Solving the Eigenvalue Problem of the Time-Independent Schrödinger Equation

The preceeding theoretical considerations shall now be put to good use. Until now, it has not been stated which operator of interest spans the Hilbert space. The time-independent

Schrödinger equation is an eigenvalue problem that applies the system's Hamiltonian (the sum of kinetic and potential energy)

$$\hat{H} = \hat{T} + \hat{V} \tag{38}$$

onto a wavefunction, returning the expectation value of the energy, the energy eigenvalue:

$$\hat{H} \ket{\Psi} = E \ket{\Psi}. \tag{39}$$

The time evolution of the system at any point is given by the time-dependent Schrödinger equation:

$$\hat{H} \ket{\Psi} = i\hbar \frac{\partial}{\partial t} \ket{\Psi} \tag{40}$$

The former is an eigenvalue problem, the latter is not.

One may rewrite the time-independent Schrödinger equation for an arbitrary state Ψ in matrix form.

$$\hat{H} \ket{\Psi} = E \ket{\Psi} \tag{41}$$

$$\sum_j c_j \hat{H} \ket{\psi_j} = E \sum_j c_j \ket{\psi_j} \tag{42}$$

All constants can be moved in front of the operator, and after multiplying by the bra $\bra{\psi_i}$, one obtains

$$\sum_j c_j \bra{\psi_i} \hat{H} \ket{\psi_j} = \sum_j H_{ij} c_j = E c_i. \tag{43}$$

Consequently, one recovers an infinite-dimensional matrix eigenvalue problem:

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1j} \\ H_{21} & H_{22} & \cdots & H_{2j} \\ \vdots & \vdots & \ddots & \vdots \\ H_{i1} & H_{i2} & \cdots & H_{ij} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_j \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_i \end{pmatrix}. \tag{44}$$

For a general matrix eigenvalue problem, there exist n solutions with eigenvalues E_k. Generalising to the above problem results in:

$$\sum_i H_{ij} c_{jk} = c_{ik} E_k. \tag{45}$$

This introduces the additional index k, and the final eigenvalue problem that is to be solved is given by:

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1j} \\ H_{21} & H_{22} & \cdots & H_{2j} \\ \vdots & \vdots & \ddots & \vdots \\ H_{i1} & H_{i2} & \cdots & H_{ij} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1k} \\ c_{21} & c_{22} & \cdots & c_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ c_{j1} & c_{j2} & \cdots & c_{jk} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1k} \\ c_{21} & c_{22} & \cdots & c_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ c_{i1} & c_{i2} & \cdots & c_{ik} \end{pmatrix} \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_k \end{pmatrix}. \tag{46}$$

The eigenvalue problem of the time-independent Schrödinger equation *can now be solved as the classical eigenvalue problem of a matrix*, by resorting to simple linear algebra.

Bosons and Fermions: Use of Determinants to Describe Many-Body Wavefunctions

Quantum mechanics imposes certain symmetry constraints on permutations of indistinguishable particles. For bosons, the wavefunction must remain unchanged upon exchange of particles. For fermions (such as electrons) instead, it has to change sign for an odd number of permutations. Formally,

$$\wp \Psi \left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \right) = \epsilon_p \Psi \left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \right), \tag{47}$$

such that $\epsilon_p = +1$ and $\epsilon_p = -1$ for an even and an odd number of permutations respectively. This poses a problem for the construction of a many-particle (many-electron) wavefunction.

If one wishes to write a many-particle wavefunction as a simple product of one-particle wavefunctions

$$\Phi \left(\mathbf{r}_1, \ldots, \mathbf{r}_N \right) = \prod_i^N \phi_i \left(\mathbf{r}_i \right), \tag{48}$$

the resulting wavefunction will be even upon permutation of a single electron:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \neq -\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) = -\Phi(\mathbf{r}_2, \mathbf{r}_1). \tag{49}$$

A simple product of single-particle wavefunctions clearly violates the permutation requirement. A determinant of a matrix, however, has exactly the desired property:

$$\det A = \begin{vmatrix} a_{11} & \cdots & a_{1N} \\ \vdots & \ddots & \vdots \\ a_{N1} & \cdots & a_{NN} \end{vmatrix} = \sum_{i=1}^{N!} (-1)^{\alpha} \, a_{1p_1} a_{2p_2} \ldots a_{Np_N}, \tag{50}$$

where α is the number of permuted pairs (p_i, p_j) with $p_i > p_j$ and $i < j$; the sum runs over all permutations $(p_1, p_2, \ldots, p_N)$ of the set $(1, 2, \ldots, N)$. Upon exchange of two columns, the determinant changes sign (which is easily demonstrated using a simple 2x2 determinant). Exploiting this property, one defines a general N-electron wavefunction:

$$\Phi \left(1, 2, \ldots, N \right) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1 \left(\mathbf{r}_1 \right) & \phi_2 \left(\mathbf{r}_1 \right) & \cdots & \phi_N \left(\mathbf{r}_1 \right) \\ \phi_1 \left(\mathbf{r}_2 \right) & \phi_2 \left(\mathbf{r}_2 \right) & \cdots & \phi_N \left(\mathbf{r}_2 \right) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1 \left(\mathbf{r}_N \right) & \phi_2 \left(\mathbf{r}_N \right) & \cdots & \phi_N \left(\mathbf{r}_N \right) \end{vmatrix} \tag{51}$$

where the ϕ_i are one-electron wavefunctions and $\frac{1}{\sqrt{N!}}$ is a normalisation factor. For a two-electron wavefunction, this reduces to

$$\Psi \left(\mathbf{r}_1, \mathbf{r}_2 \right) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1 \left(\mathbf{r}_1 \right) & \psi_2 \left(\mathbf{r}_1 \right) \\ \psi_1 \left(\mathbf{r}_2 \right) & \psi_2 \left(\mathbf{r}_2 \right) \end{vmatrix} \tag{52}$$

and

$$\Psi\left(\mathbf{r}_2, \mathbf{r}_1\right) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_2\left(\mathbf{r}_1\right) & \psi_1\left(\mathbf{r}_1\right) \\ \psi_2\left(\mathbf{r}_2\right) & \psi_1\left(\mathbf{r}_2\right) \end{vmatrix} = \Psi\left(\mathbf{r}_1, \mathbf{r}_2\right) \tag{53}$$

which is in agreement with the permutation requirement.

1.4 Exercises

The questions must be answered in your own words and have to be handed in as a written report.

1.4.1 Vectors and Matrices

a) Calculate the vector product $\mathbf{c} = \mathbf{a} \times \mathbf{b}$ with

$$\mathbf{a} = \begin{pmatrix} 2 \\ 6 \\ 4 \end{pmatrix} \quad \mathbf{b} = \begin{pmatrix} 5 \\ 1 \\ 7 \end{pmatrix} \tag{54}$$

b) and, for the same $\mathbf{a}, \mathbf{b}$, the scalar product

$$d = \mathbf{a} \cdot \mathbf{b} \tag{55}$$

c) Evaluate the matrix product

$$\begin{pmatrix} 6 & 8 & 2 \\ 9 & 1 & 5 \\ 7 & 4 & 3 \end{pmatrix} \begin{pmatrix} 9 & 6 & 7 \\ 5 & 4 & 4 \\ 3 & 2 & 8 \end{pmatrix}. \tag{56}$$

d) Evaluate the determinant for the matrix $\mathbf{A}$.

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 2 \\ 1 & 0 & 2 \\ 2 & 2 & 3 \end{pmatrix} \tag{57}$$

e) Find the eigenvalues and eigenvectors of the following matrix:

$$\begin{pmatrix} 2 & 1 \\ -1 & 4 \end{pmatrix} \tag{58}$$

f) Diagonalise these matrices. Specify which one is Hermitian.

$$\begin{pmatrix} 1 & 1-i \\ 1+i & 2 \end{pmatrix} \quad ; \quad \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix} \tag{59}$$

g) Show that if the product $\mathbf{C} = \mathbf{AB}$ of two Hermitian matrices is also Hermitian, then $\mathbf{A}$ and $\mathbf{B}$ commute.

1.4.2 A Simple Model Hamiltonian

In a system that consists of only two states (such as an electron spin in a magnetic field, where the electron spin can be in one of two orientations), the Hamiltonian has the following matrix elements: $H_{11} = a$, $H_{22} = b$, $H_{12} = d$, $H_{21} = d$. How would you determine the energy levels E and the eigenstates $\mathbf{\Psi}$ of the system? (You do not need to solve this problem explicitly, merely outlining the procedure is sufficient.)

1.4.3 Real Space Basis

a) Give the position and the momentum operators (consider only one dimension) in the position representation.

b) Give the commutator of the position and linear momentum operators in the position representation (consider one dimension only).

c) **Bonus:** Show that the potential energy operator $\hat{V}(\mathbf{r})$ is multiplicative when applied to the real-space wavefunction.

1.4.4 Commutation Relation

Explain the connection between the Heisenberg uncertainty principle and the commutation relation.
Bonus: The link between position and momentum representation is given by a Fourier transform. Explain how this relates to the Heisenberg uncertainty principle.

1.4.5 Linearity and Hermiticity

a) Is the electronic Hamiltonian $\hat{H}_{el}$ a linear operator and why (not)?

b) Does the exponent of an operator always satisfy the relation $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}$? Start from the definition of the matrix exponential.

c) **Bonus:** Prove that the eigenvalues of a Hermitian operator are real.

1.4.6 Bra-Ket Notation and State Basis

a) What is the meaning of a multiplication of a bra and a ket

$$\langle a|b\rangle , \tag{60}$$

and, conversely, an operator formed by a ket and a bra?

$$\hat{O} = |a\rangle \langle b| \tag{61}$$

b) Given a basis $\{\psi\}$ for which

$$\langle \psi_i|\psi_j\rangle = \delta_{ij}, \tag{62}$$

where δ_{ij} is the Kronecker delta, for any state Ψ

$$|\Psi\rangle = \sum_j c_j |\psi_j\rangle , \tag{63}$$

the inner product is defined as

$$\langle \Psi|\Psi\rangle = 1. \tag{64}$$

Show that this holds only as long as

$$\sum_j c_j^2 = 1, \tag{65}$$

where the c_j are the aforementioned expansion coefficients.

c) **Bonus:** Prove that, given the above conditions, $c_j = \langle \psi_j | \Psi \rangle$.

d) Show that, if two operators $\hat{A}$, $\hat{B}$ commute and if $|\psi\rangle$ is an eigenvector of $\hat{A}$, $\hat{B} |\psi\rangle$ is an eigenvector of $\hat{A}$, too, with the same eigenvalue.
Bonus: If $|\psi\rangle$ is part of a set of degenerate eigenvectors, show that the subspace spanned by the eigenvalues of $\hat{A}$ is invariant under the action of $\hat{B}$.

e) Demonstrate that, if two hermitian operators $\hat{A}$, $\hat{B}$ commute and $|\psi_1\rangle$, $|\psi_2\rangle$ are eigenvectors of $\hat{A}$ associated to different eigenvalues, then the matrix element $\langle \psi_1 | \hat{B} |\psi_2\rangle$ vanishes.

1.5 Supporting Literature

Cohen-Tannoudji, C. *et al.*: *Mécanique quantique, tome 1*. Hermann, Paris, **1997**
Specifically, chapters II(B-E), compléments D_{II} and E_{III}.