

Appendix A

A.1 Vector space and scalar product

Here we consider the vector space of all *oriented arrows* (called vectors) in the three dimensional (3D) space $\mathbb{R}^3$.

A vector space $\mathcal{V}$ on the real numbers R , is an ensemble of objects $\vec{v}_1, \vec{v}_2, \dots$ for which the operations of *addition* and *multiplication by a scalar* are specified.

For all elements, $\vec{v}_1, \vec{v}_2, \vec{v}_3$ in $\mathcal{V}$ and scalars λ, μ :

- I.
 - 1. $\vec{v}_1 + \vec{v}_2 \in \mathcal{V}$
 - 2. $\vec{v}_1 + \vec{v}_2 = \vec{v}_2 + \vec{v}_1$
 - 3. $(\vec{v}_1 + \vec{v}_2) + \vec{v}_3 = \vec{v}_1 + (\vec{v}_2 + \vec{v}_3)$
 - 4. $\exists \vec{0}$ such as $\vec{v}_1 + \vec{0} = \vec{0} + \vec{v}_1$
 - 5. $\exists$ the inverse element $-\vec{v}_1$ such as $\vec{v}_1 + (-\vec{v}_1) = \vec{0}$
- II.
 - 1. $\lambda \vec{v}_1 \in \mathcal{V}$
 - 2. $\lambda(\mu \vec{v}_1) = (\lambda\mu) \vec{v}_1$
 - 3. $(\lambda + \mu) \vec{v}_1 = \lambda \vec{v}_1 + \mu \vec{v}_1$
 - 4. $\lambda(\vec{v}_1 + \vec{v}_2) = \lambda \vec{v}_1 + \lambda \vec{v}_2$
 - 5. $\exists 1$ such as $1 \vec{v}_1 = \vec{v}_1$
 - 6. $\exists 0$ such as $0 \vec{v}_1 = \vec{0}$

In addition, we can associate to the vectorspace a **scalar product** $\vec{v}_i \cdot \vec{v}_j$ (or also $(\vec{v}_i, \vec{v}_j)$, or $\langle \vec{v}_i | \vec{v}_j \rangle$). The scalar product is a function $\mathcal{V} \times \mathcal{V} \longrightarrow \mathbb{R}$ with the following properties

- 1. $\vec{v}_1 \cdot \vec{v}_2 = \vec{v}_2 \cdot \vec{v}_1$
- 2. $\vec{v}_1 \cdot (\lambda \vec{v}_2 + \mu \vec{v}_3) = \lambda(\vec{v}_1 \cdot \vec{v}_2) + \mu(\vec{v}_1 \cdot \vec{v}_3)$

$$3. \vec{v}_1 \cdot \vec{v}_1 \geq 0$$

$$4. \vec{v}_1 \cdot \vec{v}_1 = 0 \iff \vec{v}_1 = 0$$

You know from *linear algebra* that the ensemble of all vectors in 3D is *isomorph* with the vector space $\mathbb{R}^3$, which is the ensemble of all triplets, $\{(x, y, z)\}$, that we usually call **coordinates**. However, in order to construct this isomorphism we first need to introduce a **basis**.

A.2 The Hilbert space

The Hilbert space $\mathcal{L}_2$ is the space of all complex valued functions defined in $\mathbb{R}^3$ ($f : \mathbb{R}^3 \rightarrow \mathbb{C}$) that are squared-integrable. For any $f(\mathbf{r}) \in \mathcal{L}_2$

$$\int_{\mathbb{R}^3} d^3\mathbf{r} |f(\mathbf{r})|^2 < \infty \quad .$$

In addition, for any function $f, g \in \mathcal{L}_2$ the following scalar product is defined

$$\langle f(\mathbf{r}) | g(\mathbf{r}) \rangle = \int_{\mathbb{R}^3} d^3\mathbf{r} f(\mathbf{r}) g^*(\mathbf{r}) \quad (\text{A.1})$$

with the properties

1. $\langle \phi_i | \phi_j \rangle$ is the complex conjugate of $\langle \phi_j | \phi_i \rangle$:

$$\langle \phi_i | \phi_j \rangle = \overline{\langle \phi_j | \phi_i \rangle} = \langle \phi_j | \phi_i \rangle^* . \quad (\text{A.2})$$

2. $\langle \phi_i | \phi_j \rangle$ is linear in its first argument. For all complex numbers a and b ,

$$\langle a\phi_i + b\phi_j | \phi_k \rangle = a\langle \phi_i | \phi_k \rangle + b\langle \phi_j | \phi_k \rangle . \quad (\text{A.3})$$

3. The inner product $\langle \cdot | \cdot \rangle$ is positive definite:

$$\langle \phi_i | \phi_i \rangle \geq 0 \quad (\text{A.4})$$

where the case of equality holds precisely when $\phi(x) = 0$.

It follows from properties 1 and 2 that a complex inner product is anti-linear in its second argument, meaning that

$$\langle \phi_i | a\phi_j + b\phi_k \rangle = \bar{a}\langle \phi_i | \phi_j \rangle + \bar{b}\langle \phi_i | \phi_k \rangle . \quad (\text{A.5})$$

A real inner product space is defined in the same way, except that $\mathcal{H}$ is a real vector space and the inner product takes real values. Such an inner product

will be bilinear: that is, linear in each argument. The norm defined by the inner product $\langle \cdot | \cdot \rangle$ is the real-valued function

$$||\phi(x)|| = \sqrt{\langle \phi(x) | \phi(x) \rangle}, \quad (\text{A.6})$$

and the distance between two elements $\phi_i(x)$ and $\phi_j(x)$ in $\mathcal{H}$ is defined in terms of the norm by

$$d(\phi_i(x), \phi_j(x)) = ||\phi_i(x) - \phi_j(x)|| \quad (\text{A.7})$$

A.3 The expansion in a basis set

A.3.1 Basis set in a finite vector space

Why a basis

- Once a basis is defined we can refer to any element of a vector space with its coordinates. This has enormous practical implications! Try to describe a vector sketched on a paper to somebody on another continent, without referring to a coordinate system. It is much simpler to send him the coordinates of the vector in a given coordinate system we all agree with (like the positive oriented Euclidean basis, $\{\vec{e}_1, \vec{e}_2\}$).
- All operations on the elements of the vector space can be performed with the coordinates. For example, in order to add two vectors, v_1 and v_2 , you simply have to add their coordinates

$$\vec{v} + \vec{w} = (v_1, v_2, v_3) + (w_1, w_2, w_3) = (v_1 + w_1, v_2 + w_2, v_3 + w_3)$$

The same is true for all other operations in the vector space, including the scalar product,

$$\vec{v} \cdot \vec{w} = v_1 w_1 + v_2 w_2 + v_3 w_3 \quad .$$

The question is now how to construct the coordinates for the elements of the vector space.

How to get coordinates in a given basis

A basis in a vector space is defined by a set of linear independent vectors that span the full space. In $\mathbb{R}^3$ we usually take the vectors of lengths 1, which are orthogonal to each other and are positive oriented in space. We call this basis $B = \{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$. Given a basis, the coordinates (in the basis

B) are obtained by projecting a given vector v onto the basis vectors (using the scalar product),

$$\begin{aligned}v_1 &= \vec{v} \cdot \vec{e}_1 \\v_2 &= \vec{v} \cdot \vec{e}_2 \\v_3 &= \vec{v} \cdot \vec{e}_3\end{aligned}$$

so that

$$\vec{v} = (\vec{v} \cdot \vec{e}_1) \vec{e}_1 + (\vec{v} \cdot \vec{e}_2) \vec{e}_2 + (\vec{v} \cdot \vec{e}_3) \vec{e}_3 = \sum_{i=1}^3 (\vec{v} \cdot \vec{e}_i) \vec{e}_i = \sum_{i=1}^3 v_i \vec{e}_i.$$

Some definitions

- Two vectors $\vec{v}_1$ and $\vec{v}_2$ are *orthogonal* to each other if

$$\vec{v}_1 \cdot \vec{v}_2 = 0. \quad (\text{A.8})$$

- An orthonormal basis is a complete set of linear independent vectors $\{\vec{e}_i\}$ that satisfy the condition

$$\vec{e}_i \cdot \vec{e}_j = \delta_{ij} \quad \forall i, j, \quad (\text{A.9})$$

where δ_{ij} is the Kronecker delta defined as

$$\delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases} \quad (\text{A.10})$$

- complete basis: means that any vector $\vec{v}$ in $\mathcal{V}$ can be written in the form $\vec{v} = \sum_{i=1}^N v_i \vec{e}_i$.
- linear independent set of vectors: means that one cannot write any of these vectors, say $\vec{e}_i$ as a linear combination of the other members of the set, $\{\vec{e}_j\}_{j \neq i}$.

A.3.2 Basis set in the space of 2π -periodic functions: the Fourier series

Let $f(x)$ denote a function of the real variable x . This function is usually taken to be periodic of period 2π , which is to say that $f(x + 2\pi) = f(x)$, for all real numbers x . We will attempt to write such a function as an infinite sum of simpler 2π -periodic functions. The coefficients are defined

using our scalar product in equation (A.1) adapted to the case of real periodic functions in the interval $[-\pi, \pi]$. The coefficients

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) dx, \quad n \geq 0 \quad (\text{A.11})$$

and

$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) dx, \quad n \geq 1 \quad (\text{A.12})$$

are called the Fourier coefficients of the function f . One introduces the "partial sums of the Fourier series" for f , often denoted by

$$\hat{f}_N(x) = \frac{a_0}{2} + \sum_{n=1}^N [a_n \cos(nx) + b_n \sin(nx)], \quad N \geq 0. \quad (\text{A.13})$$

The partial sums for f are trigonometric polynomials. One expects that the functions $\hat{f}_N(x)$ approximate the function f , and that the approximation improves as N tends to infinity. The infinite sum

$$\frac{a_0}{2} + \sum_{n=1}^{\infty} [a_n \cos(nx) + b_n \sin(nx)] \quad (\text{A.14})$$

is called the *Fourier series* of f .

To summarize, give a complete basis $\{\cos(nx), \sin(nx)\}_{n=1}^{\infty}$ any function $f(x)$ periodic in the interval $[-\pi, \pi]$ is uniquely described by its Fourier coefficients (array)

$$f(x) \equiv \{a_0, a_1, b_1, a_2, b_2, a_3, b_3, \dots\}. \quad (\text{A.15})$$

A.3.3 Basis functions in computational quantum chemistry

Many of the properties of vector spaces are also valid in the Hilbert space, including the existence of a basis $\{e_1(\mathbf{r}), e_2(\mathbf{r}), \dots\}$, which can be used to expand any function $f(\mathbf{r}) \in \mathcal{L}_2$

$$f(\mathbf{r}) = \sum_{i=1}^{\infty} \langle f(\mathbf{r}) | e_i(\mathbf{r}) \rangle e_i(\mathbf{r}) = \sum_{i=1}^{\infty} c_i e_i(\mathbf{r})$$

The main difference is that now the basis has an infinite number of elements. In our applications we introduce the approximation, which consists in considering only a finite number, M , of basis functions (truncation of the basis set expansion).

In quantum chemistry, any solution of the Schrödinger equation can be described by an array of coefficients $(D_1, D_2, \dots D_M)$ that defines the expansion in a given basis $(\{\phi_i(x)\})$

$$\psi(\mathbf{r}) = \sum_{i=1}^M \langle \psi(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \phi_i(\mathbf{r}) = \sum_{i=1}^{\infty} D_i \phi_i(\mathbf{r})$$

where $\{\phi_i(\mathbf{r})\}_1^M$ is, for instance, the basis set of atom-centered Gaussian orbitals.

Like for the case of vector spaces discussed above, all operations in $\mathcal{L}_2$ (like sums or multiplications of functions, scalar products, action of operators, ...) can be described and computed using the coordinates in a given basis. In particular, the Schrödinger equation for the electronic problem becomes an equation in the coefficients, D_i (the only variables in the problem).

Operators in matrix representation

Given a (complete) basis set in the position representation, $\{\phi_i(\mathbf{r})\}$, the Hamiltonian operator can be written in a matrix form

$$\hat{H} \equiv \begin{pmatrix} \langle \phi_1(\mathbf{r}) | \hat{H} | \phi_1(\mathbf{r}) \rangle & \langle \phi_1(\mathbf{r}) | \hat{H} | \phi_2(\mathbf{r}) \rangle & \dots \\ \langle \phi_2(\mathbf{r}) | \hat{H} | \phi_1(\mathbf{r}) \rangle & \langle \phi_2(\mathbf{r}) | \hat{H} | \phi_2(\mathbf{r}) \rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (\text{A.16})$$

where

$$\langle \phi_1(\mathbf{r}) | \hat{H} | \phi_1(\mathbf{r}) \rangle = \int d^3\mathbf{r} \phi_1(\mathbf{r}) \hat{H} \phi_1^*(\mathbf{r}). \quad (\text{A.17})$$

Similarly, a ket, $|\psi(\mathbf{r})\rangle$, is represented by a vector,

$$|\psi(\mathbf{r})\rangle \equiv \begin{pmatrix} \langle \phi_1(\mathbf{r}) | \psi(\mathbf{r}) \rangle \\ \langle \phi_2(\mathbf{r}) | \psi(\mathbf{r}) \rangle \\ \langle \phi_3(\mathbf{r}) | \psi(\mathbf{r}) \rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} D_1 \\ D_2 \\ D_3 \\ \vdots \end{pmatrix} \quad (\text{A.18})$$

with the meaning that

$$|\psi(\mathbf{r})\rangle = \sum_i D_i |\phi_i(\mathbf{r})\rangle. \quad (\text{A.19})$$

Within the matrix representation the problem of finding the eigenstates and energy eigenvalues of the Hamiltonian

$$\hat{H} = (\hat{T} + \hat{V}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \quad (\text{A.20})$$

is translated into the linear algebra problem of solving the matrix eigenvalue problem

$$\mathbf{H} \vec{e}_I = E_I \vec{e}_I \quad (\text{A.21})$$

where, $\mathbf{H}$ is the Hamiltonian matrix in Eq. A.16, and $\vec{e}_I$ are the eigenkets represented as in Eq. A.18. The solution is a set of energy eigenvalues, E_I , and corresponding expansion coefficients ($D_1^I, D_2^I, D_3^I, \dots$) for the eigenstates,

$$|e^I(\mathbf{r})\rangle = \sum_a D_a^I |\phi_a(\mathbf{r})\rangle. \quad (\text{A.22})$$

A.4 Properties of the operators

Adjoint operator

In mathematics, specifically in functional analysis, each linear operator on a Hilbert space has a corresponding adjoint operator. The adjoint of an operator $\hat{A}$ is also sometimes called the Hermitian conjugate of $\hat{A}$ and is denoted by $\hat{A}^*$ or $\hat{A}^\dagger$ (the latter especially when used in conjunction with the bra-ket notation).

The adjoint operator $\hat{A}^\dagger$ to the operator $\hat{A}$ is defined by

$$\langle \hat{A}\phi_i(x) | \phi_j(x) \rangle = \langle \phi_i(x) | \hat{A}^\dagger \phi_j(x) \rangle \quad \forall \phi_i, \phi_j \text{ in } \mathcal{H}. \quad (\text{A.23})$$

Self-adjoint operator (Hermitian [complex], Symmetric [real])

In mathematics, on a finite-dimensional inner product space, a self-adjoint operator is an operator that is its own adjoint.

Self-adjoint operators are used in functional analysis and quantum mechanics. In quantum mechanics their importance lies in the fact that in the Dirac-von Neumann formulation of quantum mechanics, physical observables such as position, momentum, angular momentum and spin are represented by self-adjoint operators on a Hilbert space. Of particular significance is the Hamiltonian

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V(\psi(x)) \quad (\text{A.24})$$

which as an observable corresponds to the total energy of a particle of mass m in a real potential field V .

Self-adjoint operator are defined as

$$\hat{A}^\dagger = \hat{A} \quad (\text{A.25})$$

that is

$$\langle \hat{A}\phi_i(x) | \phi_j(x) \rangle = \langle \phi_i(x) | \hat{A}\phi_j(x) \rangle \quad \forall \phi_i, \phi_j \text{ in } \mathcal{H}. \quad (\text{A.26})$$

Self-adjoint operators have *real* eigenvalues.

Unitary

A unitary operator is a linear operator $U : \mathcal{H} \rightarrow \mathcal{H}$ satisfying

$$\hat{U}^\dagger \hat{U} = \hat{U} \hat{U}^\dagger = \hat{\mathbb{I}} \quad (\text{A.27})$$

As a consequence $\hat{U}$ preserves the scalar product $\langle . | . \rangle$ of the Hilbert space, i.e., for all Hilbert space functions ϕ_i and ϕ_j in the Hilbert space, $\langle \hat{U}\phi_i | \hat{U}\phi_j \rangle = \langle \phi_i | \phi_j \rangle$.

A.4.1 Matrix notation

We have seen above that with the introduction of a basis set each operator can be described by the corresponding matrix. These matrices are in principle of infinite order, but upon truncation of the basis, we can limit ourselves to large but finite ones.

The properties discussed above become then simple matrix relations

- Self-adjoint matrix

$$A = A^\dagger \quad (\text{A.28})$$

where $A^\dagger$ is the transpose complex-conjugated of A , $A^\dagger = (A^T)^*$.

If A is real, self-adjoint is equivalent to symmetric:

$$A = A^T. \quad (\text{A.29})$$

- Unitary matrix

$$AA^\dagger = A^\dagger A = \mathbb{I} \quad (\text{A.30})$$

In the case of real matrices:

$$AA^T = A^T A = \mathbb{I} \quad (\text{A.31})$$

Example: Rotations in $\mathbb{R}^2$ are the simplest nontrivial example of unitary operators. Rotations do not change the length of a vector or the angle between 2 vectors.

In the positively oriented orthonormal basis $\vec{e}_1, \vec{e}_2$ the rotation operator has the matrix form

$$R_\theta = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}. \quad (\text{A.32})$$

Prove that $R_\theta R_\theta^T = \mathbb{I}$ (that is $R_\theta^T = R_\theta^{-1}$).

Appendix C

Hartree-Fock energy for the two electrons case

We derive the expression for the total energy of the electronic Hamiltonian

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

in the case of a 2 electrons Slater determinant wavefunction,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} |\phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2)|.$$

$$\begin{aligned}
E_{HF} &= \langle \Psi | \hat{H}_{el} | \Psi \rangle \\
&= \left(\frac{1}{\sqrt{2}} \right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 (\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \hat{H}_{el} (\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1)) \\
&= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 (\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \sum_{i=1}^N \hat{h}(i) (\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1)) \\
&\quad + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 (\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \sum_{i < j}^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} (\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1)) \\
&= \left(\frac{1}{2} \int d\mathbf{r}_1 \phi_1(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} \right) \phi_1^*(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_2(\mathbf{r}_2) \phi_2^*(\mathbf{r}_2) \right. \\
&\quad + \frac{1}{2} \int d\mathbf{r}_1 \phi_2(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} \right) \phi_2^*(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_1(\mathbf{r}_2) \phi_1^*(\mathbf{r}_2) \\
&\quad - \frac{1}{2} \int d\mathbf{r}_1 \phi_1(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} \right) \phi_2^*(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_2(\mathbf{r}_2) \phi_1^*(\mathbf{r}_2) \\
&\quad - \frac{1}{2} \int d\mathbf{r}_1 \phi_2(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} \right) \phi_1^*(\mathbf{r}_1) \int d\mathbf{r}_2 \phi_1(\mathbf{r}_2) \phi_2^*(\mathbf{r}_2) \Big) \\
&\quad + \left(\text{equivalent for } \mathbf{h}_2 \right) \\
&\quad + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 (\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} (\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1))
\end{aligned}$$

$$\begin{aligned}
E_{el} &= \sum_{i=1}^2 \langle \phi_i | \hat{h}(i) | \phi_i \rangle \\
&\quad + \frac{1}{2} \left(\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1^*(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \right. \\
&\quad - \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1^*(\mathbf{r}_2) \phi_2^*(\mathbf{r}_1) \\
&\quad - \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_2) \phi_2(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1^*(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \\
&\quad \left. + \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_2) \phi_2(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1^*(\mathbf{r}_2) \phi_2^*(\mathbf{r}_1) \right) \\
&= \sum_{i=1}^2 \langle \phi_i | \hat{h}(i) | \phi_i \rangle \\
&\quad + \frac{1}{2} \left(\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_1^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_2(\mathbf{r}_2) \phi_2^*(\mathbf{r}_2) \right. \\
&\quad - \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_2^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_2(\mathbf{r}_2) \phi_1^*(\mathbf{r}_2) \\
&\quad - \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_2(\mathbf{r}_1) \phi_1^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) \\
&\quad \left. + \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_1^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) \right) \\
&= \sum_{i=1}^2 \langle \phi_i | \hat{h}(i) | \phi_i \rangle \\
&\quad + \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_1^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_2(\mathbf{r}_2) \phi_2^*(\mathbf{r}_2) \\
&\quad - \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_1(\mathbf{r}_1) \phi_2^*(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_2(\mathbf{r}_2) \phi_1^*(\mathbf{r}_2) \\
&= \sum_{i=1}^2 \langle \phi_i | \hat{h}(i) | \phi_i \rangle + [11|22] - [12|21] \\
&= \sum_{i=1}^n \langle \phi_i | \hat{h}(i) | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^2 ([ii|jj] - [ij|ji])
\end{aligned}$$

Exercise

Derive the expression for the energy $E_H = \langle \Psi | \hat{H}_{el} | \Psi \rangle$ in the case in which the 2 electrons wavefunction is given by the Hartree product

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2)$$

When you compare with the Hartree-Fock result, E_{EH} , which term is missing?

Appendix D

Derivation of the Hartree-Fock equations

The derivation of the Fock equation consists of performing a variational calculation for the Schrödinger equation, where the subspace to which we shall confine ourselves is the space of all single Slater determinants. We must therefore calculate the expectation value of the energy for an arbitrary Slater determinant using the Born-Oppenheimer Hamiltonian and then minimize the result with respect to the spin-orbitals in the determinant. We write the Hamiltonian as follows

$$\begin{aligned}\hat{\mathcal{H}} &= \sum_i \hat{h}(i) + \frac{1}{2} \sum'_{i,j} \hat{g}(i,j) \\ \hat{h}(i) &= -\frac{\hbar}{2m} \nabla^2(i) + V(i) \\ \hat{g}(i,j) &= \frac{e^2}{r_{ij}}, \quad (r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|)\end{aligned}\tag{D.1}$$

$\hat{h}(i)$ depends on $\mathbf{r}_i$ only and $\hat{g}(i,j)$ on $\mathbf{r}_i$ and $\mathbf{r}_j$.

We start from the expectation value for the energy

$$\begin{aligned}E &= \langle \Psi^{SD}(\mathbf{r}_1, \dots, \mathbf{r}_N) | \hat{\mathcal{H}} | \Psi^{SD}(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle \\ &= \sum_k \langle \phi_k | \hat{h} | \phi_k \rangle + \frac{1}{2} \sum_{k,l} [\langle \phi_k \phi_l | \hat{g} | \phi_k \phi_l \rangle - \langle \phi_k \phi_l | \hat{g} | \phi_l \phi_k \rangle]\end{aligned}\tag{D.2}$$

We now define

$$\hat{J} = \sum_i \hat{J}_i \quad \text{and} \quad \hat{K} = \sum_i \hat{K}_i\tag{D.3}$$

where $\hat{J}_k$ and $\hat{K}_k$ are

$$\hat{J}_i \phi_k(\mathbf{r}_1) = \int \frac{|\phi_i(\mathbf{r}_2)|^2}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_2 \phi_k(\mathbf{r}_1) \quad (\text{D.4})$$

$$\hat{K}_i \phi_k(\mathbf{r}_1) = \int \frac{\phi_i^*(\mathbf{r}_2) \phi_k(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_2 \phi_i(\mathbf{r}_1) \quad (\text{D.5})$$

In terms of these operators, we can write the energy as

$$E = \sum_k \left\langle \phi_k | \hat{h} + \frac{1}{2}(\hat{J} - \hat{K}) | \phi_k \right\rangle \quad (\text{D.6})$$

This is the energy-functional for a Slater determinant. We determine the minimum of this functional as a function of the spin-orbitals ϕ_k and the set of spin-orbitals for which this minimum is reached gives us the many-electron ground state.

Notice however that the variation in the spin-orbitals ϕ_k is not completely arbitrary, but should respect the orthonormality relation:

$$\langle \phi_k | \phi_l \rangle = \delta_{kl}. \quad (\text{D.7})$$

This implies that we have a minimization problem with constraints, which can be solved using the Lagrange multiplier theorem. Note that there are only $N(N+1)/2$ independent constraints as $\langle \phi_k | \phi_l \rangle = \langle \phi_l | \phi_k \rangle^*$. Using the Lagrange multipliers Λ_{kl} for the constraints (D.7), we have

$$\delta E - \sum_{kl} \Lambda_{kl} [\langle \delta \phi_k | \phi_l \rangle + \langle \phi_k | \delta \phi_l \rangle] = 0 \quad (\text{D.8})$$

with

$$\begin{aligned} \delta E = & \sum_k \left\langle \delta \phi_k | \hat{h} | \phi_l \right\rangle + \text{c.c.} + \\ & + \frac{1}{2} \sum_{kl} (\langle \delta \phi_k \phi_l | \hat{g} | \phi_k \phi_l \rangle + \langle \phi_l \delta \phi_k | \hat{g} | \phi_l \phi_k \rangle \\ & - \langle \delta \phi_k \phi_l | \hat{g} | \phi_l \phi_k \rangle - \langle \phi_l \delta \phi_k | \hat{g} | \phi_k \phi_l \rangle) + \text{c.c.} \end{aligned}$$

Using the the following symmetry property of the two-electron matrix elements

$$\langle \phi_k \phi_l | \hat{g} | \phi_m \phi_n \rangle = \langle \phi_l \phi_k | \hat{g} | \phi_n \phi_m \rangle \quad (\text{D.9})$$

the equation for δE can be further simplified,

$$\begin{aligned} \delta E = & \sum_k \left\langle \delta \phi_k | \hat{h} | \phi_l \right\rangle + \text{c.c.} + \\ & + \sum_{kl} (\langle \delta \phi_k \phi_l | \hat{g} | \phi_k \phi_l \rangle - \langle \delta \phi_k \phi_l | \hat{g} | \phi_l \phi_k \rangle) + \text{c.c.} \end{aligned} \quad (\text{D.10})$$

Note furthermore that because of the symmetry of the constraint equations, we must have $\Lambda_{kl} = \Lambda_{kl}^*$. Eq D.10 can be rewritten as

$$\delta E = \sum_k \left\langle \delta\phi_k | \hat{\mathcal{F}} | \phi_k \right\rangle + \left\langle \phi_k | \hat{\mathcal{F}} | \delta\phi_k \right\rangle \quad (\text{D.11})$$

with

$$\left\langle \phi_k | \hat{\mathcal{F}} | \phi_l \right\rangle = \hat{h}_{kl} + \sum_{k'} [\langle \phi_k \phi_{k'} | \hat{g} | \phi_l \phi_{k'} \rangle - \langle \phi_k \phi_{k'} | \hat{g} | \phi_{k'} \phi_l \rangle] , \quad (\text{D.12})$$

and

$$\hat{\mathcal{F}} = \hat{h} + \hat{J} - \hat{K} . \quad (\text{D.13})$$

The Hermitian operator $\hat{\mathcal{F}}$ is the Fock operator formulated in terms of the operators $\hat{J}$ and $\hat{K}$. It is important to note that in this equation, $\hat{J}$ and $\hat{K}$ occur with the same pre-factor as $\hat{h}$, in contrast to Eq. D.6 in which both $\hat{J}$ and $\hat{K}$ have a factor 1/2 compared with $\hat{h}$. This extra factor is caused by the presence of two spin-orbitals in the expressions for $\hat{J}$ and $\hat{K}$ which yield extra terms in the derivative of the energy.

In this notation, the variational equation D.8 becomes

$$\left\langle \delta\phi_k | \hat{\mathcal{F}} | \phi_k \right\rangle + \left\langle \phi_k | \hat{\mathcal{F}} | \delta\phi_k \right\rangle + \sum_l \Lambda_{kl} (\langle \delta\phi_k | \phi_l \rangle + \langle \phi_l | \delta\phi_k \rangle) = 0 . \quad (\text{D.14})$$

Since $\delta\phi$ is small but arbitrary, this leads, together with $\Lambda_{kl} = \Lambda_{lk}^*$, to

$$\hat{\mathcal{F}} \phi_k = \sum_l \Lambda_{kl} \phi_l \quad (\text{D.15})$$

The Lagrange parameters Λ_{kl} in this equation cannot be chosen freely: they must be such that the solutions ϕ_k form an orthonormal set.

An obvious solution of the above equation is found by taking the ϕ_k as the eigenvectors of the Fock operators with eigenvalues ε_k , and $\Lambda_{kl} = \varepsilon_k \delta_{kl}$

$$\hat{\mathcal{F}} \phi_k = \varepsilon_k \phi_k \quad (\text{D.16})$$

where, from Eq.D.12,

$$\varepsilon_k = \langle \phi_k | \hat{\mathcal{F}} | \phi_k \rangle = \hat{h}_{kk} + \sum_{k'} [\langle \phi_k \phi_{k'} | \hat{g} | \phi_k \phi_{k'} \rangle - \langle \phi_k \phi_{k'} | \hat{g} | \phi_{k'} \phi_k \rangle] . \quad (\text{D.17})$$

We can find other solutions to the general Fock equation D.15 by transforming the set of eigenstates $\{\phi_k\}$ according to a unitary transformation

$$\phi'_k = \sum_l U_{kl} \phi_l . \quad (\text{D.18})$$

The resulting states ϕ'_k then form an orthonormal set, satisfying Eq. D.15 with

$$\Lambda_{kl} = \sum_{lm} U_{km} \varepsilon_m U_{ml}^\dagger. \quad (\text{D.19})$$

In fact, a unitary transformation of the set $\{\phi_k\}$ leaves the Slater determinant unchanged.

Equation D.15 has the form of an ordinary Schrödinger equation although the eigenvalues ε_k are identified as Lagrange multipliers rather than as energies - nevertheless they are often called 'orbital energies'.

From Eq.D.2 and Eq.D.17 it can be seen that the energy is related to the parameters ε_k by

$$E = \frac{1}{2} \sum_k \left[\varepsilon_k + \langle \phi_k | \hat{h} | \phi_k \rangle \right] \quad (\text{D.20})$$

$$= \sum_k \left[\varepsilon_k - \frac{1}{2} \langle \phi_k | \hat{J} - \hat{K} | \phi_k \rangle \right]. \quad (\text{D.21})$$

The second form shows how the Coulomb and exchange contribution must be subtracted from the sum of the Fock levels to avoid counting the two electron integrals twice.