CHAPTER 2

MANY - BODY QUANTUM MECHANICS

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CHAPTER 2

MANY-BODY QUANTUM MECHANICS

INTRODUCTION

In this chapter we introduce some of the principles of many-body quantum mechanics, applied to systems consisting of atomic nuclei and electrons. First we outline the general principles of quantum mechanics, the properties of wavefunctions and operators, which will later be used to reformulate the problem in terms of the density-matrix. We present the Born-Oppenheimer approximation used to separate the motion of the nuclei from that of the electrons, so that the problem is reduced to that of solving the equations of motion for an electron gas in a static potential. The consequences of the indistinguishability of identical particles are then discussed, as well as results of the relativistic theory of quantum mechanics which need to be included by hand in our non-relativistic treatment. Finally the powerful variational principle is introduced which is often used in solving the equations of quantum mechanics.

2.1 PRINCIPLES OF QUANTUM MECHANICS

2.1.1 Wave-functions and operators

The theory of quantum mechanics is built upon the fundamental concepts of wave-functions and operators. The wave-function is a single-valued square-integrable function of the system parameters and time which
provides a complete description of the system. Linear Hermitian operators act on the wave-function and correspond to the physical observables, those dynamical variables which can be measured, e.g. position, momentum and energy.

For systems of atomic nuclei and electrons, the system parameters might be taken to be a set of position variables of the constituent particles (the notation adopted in this and the following chapters is to refer to electronic variables using a latin index and nuclear variables with a greek index) i.e. \( |(r_1), (r_2)| \), their momenta \( |(p_1), (p_2)| \) or even a mixture of the two e.g. \( |(r_1), (p_2)| \). In contrast to a Newtonian system which is completely described by the positions and momenta of its constituents, the quantum-mechanical wave-function is a function of only one of these parameters per particle. The wave-function for the system is thus typically denoted by \( \psi(|r_1|, |r_2|, t) \).

A notation due to Dirac [64] is often employed, which reflects the fact that this wave-function is simply one of many representations of a single state-vector in a Hilbert space, which is written as \( |\psi\rangle \), known as a ket. There \( |\psi\rangle \) also exists a dual space containing a set of bra vectors, denoted \( \langle\psi| \), defined by their scalar products and in one-to-one correspondence with the kets. The scalar product is written as a bracket and is anti-linear in the first argument and linear in the second: thus \( \langle\psi|\phi\rangle = (\langle\phi|\psi\rangle)^* \). It is worth noting here that state-vectors which differ only by a multiplicative non-zero complex constant describe the same state: we can thus restrict our interest
to the set of normalised vectors defined such that the scalar product of the vector with its own conjugate equals unity:

$$\langle \psi | \psi \rangle = \int \int dr_j \int dr_\beta \psi^*(\{r_j\}, \{r_\beta\}, t) \psi(\{r_j\}, \{r_\beta\}, t) = 1 \quad (2.1)$$

The operator corresponding to some observable $O$ is often written $\hat{O}$, and in general when this operator acts on some state-vector $|\phi\rangle$, a different (not necessarily normalised) state-vector $|\phi\rangle$ results:

$$\hat{O} |\psi\rangle = |\phi\rangle. \quad (2.2)$$

However, for each operator there exists a set of normalised eigenstates, say $|\chi_n\rangle$, which remain unchanged by the action of the operator i.e.

$$\hat{O} |\chi_n\rangle = \lambda_n |\chi_n\rangle \quad (2.3)$$

in which the constant $\lambda_n$ (always real for Hermitian operators) is the eigenvalue.

The postulates of quantum mechanics [65] state that for a system in state $|\psi\rangle$:

- the outcome of a measurement of a dynamical variable is always one of the eigenvalues $\lambda_n$ of the corresponding operator,
- immediately following a measurement, the state-vector collapses to the eigenstate $|\chi_n\rangle$ corresponding to the measured eigenvalue,
- the probability of such a measurement is

$$P(\lambda_n) = |\langle \chi_n | \psi \rangle|^2$$
2.1.2 Expectation values

Much of the power of the theory comes from the fact that the quantum-mechanical states can be linearly superposed since this leads to no ambiguity in the action of linear operators. We now consider the quantity $\langle \psi | \hat{O} | \psi \rangle$. From Sturm-Liouville theory, the eigenstates of the operator $\hat{O}$ form a complete set, which means that any valid state-vector can be expressed as a linear superposition of those eigenstates with appropriate complex coefficients $\{c_n\}$:

$$\left| \psi \right> = \sum_n C_n \left| \chi_n \right>$$  \hspace{1cm} (2.5)

These coefficients are easily obtained for Hermitian operators because the eigenstates are orthogonal (or can always be chosen to be orthogonal in the case of degenerate eigenvalues) which means that the scalar product of two different eigenstates vanishes:

$$\langle \chi_n | \chi_m \rangle = \delta_{nm}$$  \hspace{1cm} (2.6)

Either taking scalar products of both sides of eq. (2.5) with the eigenstates $\left| \langle \chi_m \right| 1$, or by using the following concise expression of completeness;

$$\sum_n \left| \chi_n \right> \langle \chi_n | = 1$$  \hspace{1cm} (2.7)

the expansion coefficients $\{C_n\}$ can be determined:

$$C_n = \langle \chi_n | \psi \rangle$$  \hspace{1cm} (2.8)
\[ |\psi\rangle = \sum_n |\chi_n\rangle \langle \chi_n | \psi \rangle \]  

(2.9)

Now this result is applied to the quantity \( \langle \psi | \hat{O} | \psi \rangle \):

\[
\langle \psi | \hat{O} | \psi \rangle = \sum_m (\langle \chi_m | \psi \rangle)^* \langle \chi_m | \hat{O} \rangle \sum_n |\chi_n\rangle \langle \chi_n | \psi \rangle = \sum_n \lambda_n |\langle \chi_n | \psi \rangle|^2
\]

in which we have used the fact that \( \hat{O} \) is linear, that the \( |\chi_n\rangle \) are eigenstates of \( \hat{O} \) eq. (2.3) and the orthonormality relation eq. (2.6).

Since the only possible outcomes of a measurement of the observable \( O \) corresponding to operator \( \hat{O} \) are the eigenvalues \( (\lambda_n) \), with corresponding probabilities \( |\langle \chi_n | \psi \rangle|^2 \) eq. (2.4), the quantity \( \langle \psi | \hat{O} | \psi \rangle \) is to be interpreted as the expectation value of \( O \) for a system in state \( |\psi\rangle \). The normalisation condition \( \langle \psi | \psi \rangle = 1 \) corresponds to the condition that the probabilities sum to unity.

### 2.1.3 Stationary states

The final postulate of quantum mechanics states that between measurements, the state-vector evolves in time according to the time-dependent Schrödinger equation:

\[
H |\psi\rangle = i \frac{\partial}{\partial t} |\psi\rangle
\]

(2.11)
This treatment is non-relativistic: for heavy atoms there are significant relativistic effects but these can be incorporated a posteriori in the construction of the pseudopotentials. The operator $\hat{H}$ is known as the Hamiltonian and is the energy operator, which for systems of atomic nuclei and electrons takes the form

$$\hat{H} = -\sum_{i} \nabla_{i}^{2} - \sum_{\alpha} \frac{1}{2m_{\alpha}} \sum_{\alpha} \frac{Z_{\alpha}}{|r_{i} - r_{\alpha}|}$$

$$+ \sum_{i \neq j} \frac{1}{|r_{i} - r_{j}|} + \sum_{\alpha \neq \beta} \frac{Z_{\alpha}Z_{\beta}}{|r_{\alpha} - r_{\beta}|}$$

(2.12)

in which the nuclear masses $m_{\alpha}$ and atomic numbers $Z_{\alpha}$ appear. The first two terms on the right-hand side represent the kinetic energies of the electrons and nuclei respectively. The subsequent terms describe the electron-nuclear, electron-electron and inter-nuclear Coulomb interaction energies respectively.

Finally we note that if we solve the time-independent Schrödinger equation, the eigenvalue equation for the Hamiltonian, then the time-dependence of the wave-function takes a particularly simple form. The following separation of variables is made:

$$\psi(r_{i}, r_{j}, t) = \tilde{\psi}(s(1, r_{i})) \Theta(t)$$

(2.13)

which is successful and leads to the following equations, where $E$ is the separation constant:
The ordinary differential eq. (2.15) is straightforwardly solved, so that eigenfunctions of the Hamiltonian with energy \( E \) take the form:

\[
\psi ((r,),(r,),(t)) = \tilde{\psi} ((r,),(r,)) \exp(-iEt) \tag{2.16}
\]

States which are eigenfunctions of the Hamiltonian are also known as stationary states because the expectation values of time-independent operators for these states are also independent of time:

\[
\langle \psi | \hat{O} | \psi \rangle = \int \cdots dr_{\alpha} \cdots dr_{\beta} \tilde{\psi}^{*} ((r,),(r,)) \hat{O} \psi ((r,),(r,))
\]

\[
= \int \cdots dr_{\alpha} \cdots dr_{\beta} \tilde{\psi}^{*} ((r,),(r,)) \exp(iEt) \hat{\tilde{O}} \tilde{\psi} ((r,),(r,)) \exp(-iEt)
\]

\[
= \langle \tilde{\psi} | \hat{O} | \tilde{\psi} \rangle \tag{2.17}
\]

From now on we shall be dealing with eigenstates of the Hamiltonian, and so will suppress the exponential time-dependence of the state and deal directly with the time-independent state \( | \tilde{\psi} \rangle \) instead.
2.2 THE BORN-OPPENHEIMER APPROXIMATION

The forces on both electrons and nuclei due to their electric charge are of the same order of magnitude, and so the changes which occur in their momenta as a result of these forces must also be the same. One might, therefore, assume that the actual momenta of the electrons and nuclei were of similar magnitude. In this case, since the nuclei are so much more massive than the electrons, they must accordingly have much smaller velocities. Thus it is plausible that on the typical time-scale of the nuclear motion, the electrons will very rapidly relax to the instantaneous ground-state configuration, so that in solving the time-independent Schrödinger equation resulting from the Hamiltonian in eq. (2.12), we can assume that the nuclei are stationary and solve for the electronic ground-state first, and then calculate the energy of the system in that configuration and solve for the nuclear motion. This separation of electronic and nuclear motion is known as the Born-Oppenheimer approximation [66].

Following Ziman [67], we assume the following form of an eigenfunction for the Hamiltonian eq. (2.12):

$$\tilde{\psi}([r_i], [r_a]) = \psi([r_i], [r_a]) \phi([r_a])$$  \hspace{1cm} (2.18)

and require that $\psi([r_i], [r_a])$ (which is a wave-function only of the $[r_i]$ with the $[r_a]$ as parameters) satisfies the time-independent Schrödinger equation for the electrons in a static array of nuclei:
in which the dependence of the eigenvalues \( \varepsilon_i \) on the nuclear positions is acknowledged. Applying the full Hamiltonian eq. (2.12) to the whole wavefunction:

\[
\hat{H}\psi(r_i; r_{\alpha}) = -\sum_{\beta} \frac{1}{2m_\beta} \nabla_\beta^2 + \varepsilon_\beta(r_{\alpha}) + \frac{1}{2} \sum_{\gamma \neq \beta} \sum_{i} \frac{Z_\alpha}{|r_i - r_\alpha|} + \sum_{\beta} \frac{1}{2m_\beta} \nabla_\beta^2 + \varepsilon_\beta(r_{\alpha}) + \frac{1}{2} \sum_{\gamma \neq \beta} \sum_{i} \frac{Z_\alpha Z_\gamma}{|r_\beta - r_\gamma|} - \sum_{\beta} \frac{1}{2m_\beta} \nabla_\beta^2 + \varepsilon_\beta(r_{\alpha}) + \frac{1}{2} \sum_{\gamma \neq \beta} \sum_{i} \frac{Z_\alpha Z_\gamma}{|r_\beta - r_\gamma|} - \phi(r_{\alpha})
\]

The energy \( \varepsilon_\alpha(r_{\alpha}) \) is called the adiabatic contribution of the electrons to the energy of the system. The remaining non-adiabatic terms contribute very little to the energy, which can be demonstrated using time-independent perturbation theory [68]. The first order correction arising from the first non-adiabatic term in the last line of eq. (2.20) is of the form:

\[
\sum_{\beta} \frac{1}{2m_\beta} \left[ 2\nabla_\beta \phi(r_{\alpha}) \cdot \nabla_\beta \psi(r_i; r_{\alpha}) + \phi(r_{\alpha}) \nabla_\beta^2 \psi(r_i; r_{\alpha}) + \phi(r_{\alpha}) \nabla_\beta^2 \psi(r_i; r_{\alpha}) \right]
\]
and the term in square brackets can be rewritten

\[
\int_j dr_j \psi^\ast (\{r_j\}; \{r_a\}) \nabla_j \psi (\{r_j\}; \{r_a\}) = -\frac{1}{2} \nabla \int_j dr_j |\psi (\{r_j\}; \{r_a\})|^2
\]

\[
= -\nabla, 1 = 0, \quad (2.21)
\]

since the normalisation of the electronic wave-function does not change when the nuclei move, so that the first order contribution vanishes. The second-order shift due to this term does not vanish and gives rise to transitions between electronic states as the ions move, otherwise known as the electron-phonon interaction, which will modify the energy.

The second non-adiabatic term in the final term of eq. (2.20) will be largest when the electrons labelled i are tightly bound to the nuclei labelled \( \alpha \) in which case \( \psi (\{r_i\}; \{r_a\}) = \psi (\{u_{i,\alpha}\}) \) where \( u_{i,\alpha} = r_i - r_a \) and the first order correction from this term is

\[
- \int_j dr_j \psi^\ast (\{u_{i,\alpha}\}) \phi^\ast (\{r_a\}) \sum_\gamma \frac{1}{2m_r} \nabla_\gamma \psi (\{u_{i,\alpha}\})
\]

\[
= -\frac{1}{2m_r} \int_i \beta \phi (\{r_a\}) |^2 \int_{(i,\beta)} dn_{i,\beta} \psi (\{u_{i,\beta}\}) \nabla_\beta \psi (\{u_{i,\beta}\})
\]
and this quantity is of the order of the electronic kinetic energy multiplied by the ratio of the electron and nuclear masses, typically a factor of the order of \(10^4\) or \(10^5\), so that the contributions from this term to all orders can be neglected.

We therefore neglect the non-adiabatic terms and note that eq. (2.20) is satisfied if \(\phi\left(|r_o\rangle\right)\) obeys a Schrödinger equation of the form

\[
\sum_{\beta} \frac{1}{2m_o} \nabla_{\beta}^2 \epsilon_{\alpha}(|r_o\rangle) \frac{1}{2} - \sum_{\beta} \sum_{r\neq\beta} \frac{Z_oZ_{\beta}}{|r_{\beta}-r_r|} \phi(|r_o\rangle) = \epsilon \phi(|r_o\rangle)
\]  

This adiabatic principle is crucial because it allows us to separate the nuclear and electronic motion, leaving a residual electron-phonon interaction. From this point on it is assumed that the electrons respond instantaneously to the nuclear motion and always occupy the ground-state of that nuclear configuration. Varying the nuclear positions maps out a multi-dimensional ground-state potential energy surface, and the motion of the nuclei in this potential can then be solved. In practice Newtonian mechanics generally suffices for this part of the problem and relaxation of the nuclear positions to the minimum-energy configuration or molecular dynamics [69,70] can be performed. These aspects go beyond the scope of this thesis so that from now on it is assumed that a system with a fixed nuclear configuration is to be treated, so that the electronic energy \(\epsilon_{\alpha}\) is a
constant and the electronic wave-function $\psi(r_a)$ obeys the Schrödinger eq. (2.19). The dependence of the electronic wave-function on the nuclear positions $\{r_a\}$ is now suppressed.

2.3 IDENTICAL PARTICLES

2.3.1 Symmetries

It is a consequence of quantum mechanics, usually expressed in the terms of the Heisenberg uncertainty principle that, in contrast to Newtonian mechanics, the trajectory of a particle is undefined. When dealing with identical particles this leads to complications.

Consider a system of two identical particles represented by the wave-function $\psi(r_1, r_2)$ and a particle-exchange operator $\hat{P}_{12}$ which swaps the particles i.e.

$$\hat{P}_{12}\psi(r_1, r_2) = \psi(r_2, r_1) \quad (2.24)$$

However, since the system must be unchanged by such an exchange of identical particles, the two states appearing in eq. (2.25) must be the same and hence differ only by a multiplicative complex constant;

$$\psi(r_2, r_1) = c\psi(r_1, r_2) \quad (2.25)$$

so that many-body wave-functions of identical particles must be eigenstates of the particle interchange operator. Performing the exchange twice clearly returns the system precisely to its original state and so leads to

$$\hat{P}_{12}^2\psi(r_1, r_2) = C^2\psi(r_1, r_2) = \psi(r_1, r_2) \quad (2.26)$$
i.e. $C^2 = 1$. So $C = \pm 1$, and the many-body wave-function at most changes sign under particle exchange. This result is readily extended to systems of more than two identical particles, so that the wave-functions are either symmetric or antisymmetric under exchange of any two identical particles.

### 2.3.2 Spin and statistics

It is necessary to go to the full relativistic theory of quantum mechanics in order to ascertain which sign is appropriate to a system of particles, although the result itself is simple enough to express. A result of the relativistic theory is that particles may possess intrinsic angular momentum known as spin, which is quantised in units of $\frac{1}{2}$. A brief outline of the relationship between spin and statistics follows.

We use the method of second quantisation of fields of particles with spin. For a system of free non-interacting particles, the single-particle states are characterised by linear momentum $P$ and $\sigma$. We denote the occupation numbers of these states $N_{p\sigma}$, but for now we will only consider situations in which every single-particle state is either empty or singly occupied, and in addition will consider a system of at most two particles and focus on just two single-particle states. The state-vector is represented by a series of "slots", whose order is important at this stage, each containing an occupation number. Thus $|1_{p\sigma}, 1_{p\sigma}\rangle$ denotes a state in which a particle was put in state $(p\sigma')$ and then a second particle was added in state $(p\sigma)$.
Annihilation and creation operators $\hat{a}_{p\sigma}$, $\hat{a}^*_{p\sigma}$ are introduced for each state which act in the following manner:

$$\hat{a}_{p\sigma} |11\rangle_{p\sigma} = |0\rangle_{p\sigma},$$  
$$\hat{a}^*_{p\sigma} |0\rangle_{p\sigma} = |1\rangle_{p\sigma}$$  

(2.27)  
(2.28)

In order that the sign of the state is unambiguously defined in this notation, it is necessary for consistency that creation operators act on the right-most void and annihilation operators act on the left-most appropriately-filled slot.

We now consider the state $|1_{p\sigma}, 1_{p'\sigma}'\rangle$ and use the exchange operator $\hat{a}_{p'\sigma}^* \hat{a}_{p\sigma}^\dagger \hat{a}_{p'\sigma} \hat{a}_{p\sigma}$ to obtain the state $|1_{p'\sigma}, 1_{p\sigma}\rangle$, in which particles have been exchanged between state $(p\sigma)$ and $(p'\sigma')$:

$$\hat{a}_{p'\sigma}^* \hat{a}_{p\sigma}^\dagger \hat{a}_{p'\sigma} \hat{a}_{p\sigma} |1_{p\sigma}, 1_{p'\sigma}\rangle = \hat{a}_{p'\sigma}^* \hat{a}_{p\sigma}^\dagger |1_{p\sigma}, 0\rangle = \hat{a}_{p'\sigma}^* \hat{a}_{p\sigma}^\dagger |0,0\rangle = \hat{a}_{p\sigma}^\dagger |0,1_{p\sigma}\rangle = |1_{p'\sigma}, 1_{p\sigma}\rangle$$  

(2.29)

The initial discussion in this section showed that under this exchange, the wave-function at most changes sign. This requires that the creation and annihilation operators obey one of two sets of commutation rules, as we will now show. The first set is due to Bose and can be summarised by:

$$[\hat{a}_{p'\sigma}^*, \hat{a}_{p\sigma}] = \delta_{pp'}, \delta_{\sigma\sigma}$$  
$$[\hat{a}_{p\sigma}, \hat{a}_{p'\sigma}] = 0$$  
$$[\hat{p}, \hat{q}] = \hat{p} \hat{q} - \hat{q} \hat{p}$$  

(2.30)  
(2.31)  
(2.32)
Under the Bose commutation rules, the two creation operators in the exchange operator, which refer to different states, commute and so can be swapped, and the result is that

\[
\hat{a}^\dagger_{p,\sigma} \hat{a}^\dagger_{p,\sigma'} a_{p\sigma} a_{p'\sigma'} |1_{p\sigma}, 1_{p'\sigma'}\rangle = |1_{p'\sigma'}, 1_{p\sigma}\rangle
\]

\[
= a_{p\sigma} a^\dagger_{p,\sigma'} \hat{a}^\dagger_{p,\sigma} a_{p'\sigma'} |1_{p\sigma}, 1_{p'\sigma'}\rangle = |1_{p\sigma}, 1_{p'\sigma'}\rangle
\]  

(2.33)

i.e. states describing particles whose creation and annihilation operators obey the Bose commutation rules (bosons) must have symmetric wave-functions.

The second set of commutation rules, which is due to Fermi, describes fermions:

\[
|a_{p\sigma}, \hat{a}^\dagger_{p,\sigma}\rangle = \delta_{pp}, \delta_{\sigma\sigma'}
\]  

(2.34)

\[
|a_{p\sigma}, a^\dagger_{p,\sigma}\rangle = 0
\]  

(2.35)

where

\[
|p, q\rangle = \hat{p}^\dagger \hat{q}^\dagger
\]  

(2.36)

and gives rise to antisymmetric wave-functions:

\[
\hat{a}^\dagger_{p,\sigma} a^\dagger_{p,\sigma'} a_{p\sigma} a_{p'\sigma'} |1_{p\sigma}, 1_{p'\sigma'}\rangle = |1_{p'\sigma'}, 1_{p\sigma}\rangle
\]

\[
= -a^\dagger_{p,\sigma} a^\dagger_{p,\sigma'} a_{p\sigma} a_{p'\sigma'} |1_{p\sigma}, 1_{p'\sigma'}\rangle = -|1_{p\sigma}, 1_{p'\sigma'}\rangle
\]  

(2.37)

In particular, note that the Fermi rules (eq. (2.36) for \((p\sigma) = (p'\sigma'|)\) require that

\[
\hat{a}_{p\sigma} a_{p\sigma} = a^\dagger_{p\sigma} a^\dagger_{p\sigma} = 0
\]  

(2.38)
i.e. it is impossible to put more than one fermion in any single-particle state. This result is known as the Pauli exclusion principle and it is ultimately responsible for the stability of matter. In an atom, for instance, the Pauli exclusion principle prevents all of the electrons from falling into the lowest-lying energy level.

Thus all systems of identical particles must subscribe to one of the sets of rules above; bosons have symmetric wave-functions and fermions antisymmetric wave-functions.

The second result of the relativistic theory which needs to be considered is the existence of antiparticles, which have the same mass but opposite charge to their corresponding particles. The antiparticles are assigned their own set of creation and annihilation operators, denoted \( \hat{b}^\ast_{-p\sigma} \) and \( \hat{b}_{-p\sigma} \), respectively, which obey the same commutation rules as the particle operators.

The creation and annihilation operators can be combined to form a Hermitian product, the number operator, \( \hat{N}_{p\sigma} = \hat{a}_{-p\sigma}^\dagger \hat{a}_{-p\sigma} \), so-called because its action is simply to return the number of particles in state \((p\sigma)\). For antiparticles, \( \hat{N}_{-p\sigma} = \hat{b}_{-p\sigma}^\dagger \hat{b}_{-p\sigma} \).

Using the method of second quantisation, the Hamiltonian can be written as:

\[
\hat{H} = \sum_p \sum_\sigma \epsilon(P) \left( \hat{a}_{-p\sigma}^\dagger \hat{a}_{p\sigma} \pm \hat{b}_{-p\sigma}^\dagger \hat{b}_{p\sigma} \right)
\]  

(2.39)
where the $\varepsilon(p) = \sqrt{p^2 + m^2}$ are the energies of the single-particle states, and the plus sign occurs for particles of integral spin and the minus sign for particles with half-integral spin. We note that the particle creation and annihilation operators occur in the correct order to be written as the particle number operator, whereas the antiparticle operators are in the wrong order, so we can use the appropriate set of communication rules to reverse this order. The Hamiltonian for free particles must be positive-definite, and therefore turns out to be of the form

$$\hat{H} = \sum_p \sum_\sigma \varepsilon(p) (N_{p\sigma} + N_{p\bar{\sigma}} + 1)$$  \hspace{1cm} (2.40)

The constant $\sum_p \sum_\sigma \varepsilon(p)$ in eq. (2.41) represents the energy of the vacuum and is usually ignored. In order to obtain the Hamiltonian in this form, particles with half-integral spin (minus sign in eq. 2.40) must have creation and annihilation operators which anticommute according to the Fermi rules, whereas particles with integral spin (plus sign in eq. 2.40) must have operators which commute according to the Bose rules.

We thus come to the following conclusions:

- particles with half-integral spin are fermions and have antisymmetric wave-functions.
- particles with integral spin are bosons and have symmetric wave-functions.
In particular, electrons (which have spin 1/2) are fermions with antisymmetric wave-functions and obey the Pauli exclusion principle. These consequences of relativistic quantum mechanics must be carried over by hand into the non-relativistic theory if we are to correctly describe nature.

In this dissertation we will not address the issues which arise in spin-polarised systems, in which the numbers of electrons in different spin states differ. In our case, it is only necessary to ensure that the many-body electronic wave-function is antisymmetric under exchange and that each single-particle state is never more than doubly-occupied (with one spin "up" electron and one spin "down").

2.4 VARIATIONAL PRINCIPLES

In section 2.1 we outlined the basic principles of quantum mechanics, and in particular noted the role of the quantity $\langle \psi | \hat{O} | \psi \rangle$ as the expectation value of the observable corresponding to the operator $\hat{O}$. In that section, mention was briefly made of the relationship:

$$\langle \psi | \psi \rangle = \sum_n |\langle \chi_n | \psi \rangle|^2 \quad (2.41)$$

which is simply derived from (eqns. 2.5, 2.6 and 2.8). If we relax the restriction on orthonormalisation, the expression for the expectation value becomes

$$\langle O \rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (2.42)$$
We now consider the expectation value of the Hamiltonian operator for the electrons, defined in eq. (2.19) and reproduced here:

\[ \hat{H} | \psi \rangle = \left[ -\frac{1}{2} \sum_i V_i^2 - \sum_a \frac{Z_a}{|r_i - r_a|} + \frac{1}{2} \sum_j \sum_{j \neq i} \frac{1}{|r_i - r_j|} \right] | \psi \rangle = E | \psi \rangle \tag{2.43} \]

in which the electronic energy is now labelled E, and the dependence on the nuclear coordinates is suppressed since the nuclei are assumed to be static following the conclusions of section 2.2. This equation is an eigenvalue equation for a linear Hermitian operator, and as such can always be recast in the form of finding the stationary points of a functional subject to a constraint.

Consider the expectation value of the Hamiltonian \( \langle E \rangle = E[\psi] \) which is a functional of the wave-function, and make a small variation to the state-vector: \( | \psi \rangle \rightarrow | \psi \rangle + | \delta \psi \rangle \). The change in \( F | \psi \rangle \) is given by

\[
\delta E[\psi] = E[\psi + \delta \psi] - E[\psi] = \frac{\langle \psi + \delta \psi | \hat{H} | \psi + \delta \psi \rangle - \langle \psi | \hat{H} | \psi \rangle}{\langle \psi + \delta \psi | \psi + \delta \psi \rangle - \langle \psi | \psi \rangle} - \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \]

\[
= \frac{\langle \delta \psi | \hat{H} | \psi \rangle + \langle \psi | \hat{H} | \delta \psi \rangle - \langle \psi \rangle}{\langle \psi \rangle} - \frac{\langle \delta \psi | \psi \rangle + \langle \psi | \delta \psi \rangle}{\langle \psi \rangle^2} + O(\delta \psi^2)
\]

\[
= \frac{1}{\langle \psi | \psi \rangle} \left[ \langle \delta \psi | \hat{H} | \psi \rangle - E[\psi] | \psi \rangle + \{ \langle \delta \psi | \hat{H} | \psi \rangle - E[\psi] | \psi \rangle \}^* \right] \tag{2.44}
\]
neglecting changes which are second-order or higher in $\delta \psi$ in the last line. Thus the quantity $E[\psi]$ is stationary ($\delta E[\psi] = 0$) when $|\psi\rangle$ is an eigenstate of $\hat{H}$ and the eigenvalue is $E[\psi]$,

\[ \hat{H} |\psi\rangle = E[\psi] |\psi\rangle \]  

and this equation is the time-independent Schrödinger equation. The eigenvalues of $\hat{H}$ can therefore be found by finding the stationary values of $E[\psi]$ i.e. finding the stationary values of $\langle \psi | \hat{H} | \psi \rangle$ subject to the constraint that $\langle \psi | \psi \rangle$ is constant. In this procedure, the eigenvalue $E$ plays the role of a Lagrange multiplier used to impose the constraint.

In this thesis we will only be interested in finding the electronic ground-state $|\psi_0\rangle$ which is the eigenstate of the Hamiltonian with the lowest eigenvalue $E_\nu$. Suppose that we have a state close to the ground-state, but with some small error. Since the eigenstates of the Hamiltonian form a complete set, the error can be expanded as a linear combination of the excited eigenstates. The whole state can thus be written as

\[ |\psi\rangle = |\psi_0\rangle + \sum_{n=1}^{\infty} C_n |\psi_n\rangle \]  

where

\[ \hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \]  

We now calculate the value of $E[\psi]$:

\[ E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \]
\[
\langle \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n | \hat{H} | \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n \rangle = \\
\langle \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n | \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n \rangle \\
\langle \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n | E_0 \psi_0 + \sum_{n=1}^{\infty} C_n \psi_n \rangle = \\
E_0 + \sum_{n=1}^{\infty} |C_n|^2 E_n \\
1 + \sum_{n=1}^{\infty} |C_n|^2 \\
= E_0 + \sum_{n=1}^{\infty} |C_n|^2 (E_n - E_0) + O (|C_n|^4) \\
\text{(2.48)}
\]

By definition, \(E_0 > E_0\) for \(n \geq 1\), so that we note two points:

- \(E[\psi] \geq E_0\), with equality only when \(|\psi\rangle = |\psi_0\rangle\) (i.e. \(C_n = 0\) for \(n \geq 1\)).
- the error in the estimate of \(E_0\) is second-order in the error in the wave-function (i.e. \(C_n\)).

The importance of such a variational principle is now clear. To calculate the ground-state energy \(E_0\), we can minimise the functional \(E[\psi]\) with respect to all states \(|\psi\rangle\) which are antisymmetric under exchange of particles. The value of this functional gives an upper bound to the value of \(E_0\) and even
a relatively poor estimate of the ground-state wave-function gives a relatively good estimate of $E_0$. Eigenstates corresponding to excited states of the Hamiltonian can be found by minimising the functional with respect to states which are constructed to be orthogonal to all lower-lying states (which is usually achieved by considering the symmetries of the states) but in this work we will only ever be interested in the ground-state, and so there are no restrictions on the states other than antisymmetry.