

Advanced Quantum Mechanics: Course Summary

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Introduction

This guide accompanies my Year 4 course “*Advanced Quantum Mechanics*”. It is a summary of the main results which is intended to

- emphasise which results are more fundamental or are applications of especially wide significance;
- reiterate the structure of the course;
- provide a convenient reference to earlier results when learning the later parts of the course or doing problems.

It is *not* a comprehensive description of the course, and should not be taken to imply which material is examinable. Equally, it is not a list of results that have to be memorised: many of the results here may (with practice) be derived quite easily from a small number of the most fundamental principles.

It is not intended to be a self-contained document. For example, the definitions of some symbols and quantities are not given (but are, of course, to be found in your lecture notes or a textbook). Do remember also the useful departmental Table of Constants and Mathematical Formulae (as provided to students in exams), which is available on the Physics Wiki page <https://wiki.york.ac.uk/display/Physics/Assessment+and+Feedback>.

I'd welcome any suggestions for additions or other changes.

1 Time-Dependence

1.1 Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi.$$

1.2 Cases (a) and (b): Time-independent Hamiltonian

Case (a): If the system is in an eigenstate ϕ_j of the Hamiltonian at time $t = 0$,

$$\psi(\mathbf{r}, t) = e^{-iE_j t/\hbar} \phi_j(\mathbf{r}).$$

Case (b): If the system is in a general quantum state at time $t = 0$, which is given in terms of the eigenfunctions ϕ_j as

$$\psi(\mathbf{r}, t=0) = \sum_j c_j \phi_j(\mathbf{r}),$$

then, because we may superpose solutions for a linear differential equation,

$$\psi(\mathbf{r}, t) = \sum_j c_j e^{-iE_j t/\hbar} \phi_j(\mathbf{r}).$$

1.3 Case (c): Time-dependent Hamiltonian; Time-dependent perturbation theory

The wavefunction of a system is initially an eigenfunction, ϕ_s , of its time-independent Hamiltonian \hat{H}_0 with energy E_s . At time $t = 0$ the Hamiltonian acquires an additional time-dependent part $\Delta\hat{H}(\mathbf{r}, t)$. The wavefunction at a later time is to be written in terms of the eigenfunctions ϕ_j and eigenvalues E_j of the unperturbed Hamiltonian \hat{H}_0 as

$$\psi(\mathbf{r}, t) = \sum_j c_j(t) e^{-iE_j t/\hbar} \phi_j(\mathbf{r}).$$

We used the time-dependent Schrödinger equation to show that the coefficients c_k ($k \neq s$) are given, to first order in $\Delta\hat{H}$, by¹

$$c_k(t) = \frac{1}{i\hbar} \int_{t'=0}^t e^{+i\omega_{ks}t'} \langle \phi_k | \Delta\hat{H}(\mathbf{r}, t') | \phi_s \rangle dt',$$

where $\omega_{ks} = (E_k - E_s)/\hbar$. This is the result for first-order time-dependent perturbation theory (i.e. first order in $\Delta\hat{H}$).

In the case where the perturbing Hamiltonian takes the oscillatory form $\Delta\hat{H}(\mathbf{r}, t) = \Delta V(\mathbf{r}) \cos(\omega_0 t)$ ($t > 0$), we derived **Fermi's golden rule** for the probability of being in a final state k with energy $E_k = E_s + \hbar\omega_0$,

$$P = \frac{\pi t}{2\hbar} |\langle \phi_k | \Delta V(\mathbf{r}) | \phi_s \rangle|^2 g(E_k),$$

where g is the density of states at the energy mentioned, corresponding to absorption. (There is, of course, a corresponding expression for $E_k = E_s - \hbar\omega_0$, stimulated emission.)

Selection rules arise from the fact that some transition rate are zero (at least in first-order TDPT), by virtue of the symmetry of the matrix element

1.4 Ehrenfest's theorem

Starting from the time-dependent Schrödinger equation, we showed that, if \hat{A} is an Hermitian operator, and \hat{H} is the Hamiltonian, then the rate of change of the expectation value of the corresponding variable is

$$\frac{d}{dt} \langle \hat{A} \rangle = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle.$$

2 The Classical Limit

Using Ehrenfest's theorem is it easy to prove that

$$\frac{d}{dt} \langle \hat{p} \rangle = \langle f \rangle,$$

¹Reminder of the Dirac notation which I often use: $\langle \phi_k | \Delta\hat{H}(\mathbf{r}, t') | \phi_s \rangle$ stands for $\int \phi_k^*(\mathbf{r}) \Delta\hat{H}(\mathbf{r}, t') \phi_s(\mathbf{r}) d^3r$, where the integral is over all space

where f is the force operator $-\frac{\partial V}{\partial x}$, and

$$\frac{d}{dt} \langle x \rangle = \frac{\langle \hat{p} \rangle}{m},$$

which together comprise

$$m \frac{d^2}{dt^2} \langle x \rangle = \langle f \rangle.$$

In the limit when a wavepacket becomes sufficiently localised in space, and sufficiently well-defined in momentum, that each expectation value may both be replaced by “the” value, this is Newton’s second law $F = m\ddot{x}$: classical mechanics.

3 Many-particle Quantum Mechanics

3.1 Generalised Pauli principle

For a system of identical bosons, Ψ must be *symmetric* with respect to exchange of any pair of particle coordinates, and for fermions, *antisymmetric*. We shall mostly talk about fermions here. For identical *non-interacting* fermions, this leads to the familiar requirement that each single-particle state (describing the spatial and spin parts of the single-particle wavefunction) cannot be occupied by more than one fermion.

3.2 Many-particle wavefunctions

The Hamiltonian for an atom comprising two interacting electrons plus a fixed nucleus of atomic number Z takes the form

$$\hat{H} = \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 \right] + \left[-\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right] + \left[\frac{\lambda e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right]$$

where the constant λ normally has the value 1.

The terms in square brackets represent, respectively, the kinetic energy of the two electrons, the potential energy of the two electrons due to their attraction to the nucleus, and the potential energy of the two electrons due to their mutual repulsion. (For atoms with more electrons, the last term would involve a sum over all pairs of electrons, counting each pair just once.)

Finding the eigenfunctions of this Hamiltonian is already very hard; in particular it cannot be done analytically. But *if we ignored interaction* by setting $\lambda = 0$, it would become far simpler, because the method of separation of variables can be used to separate the N -electron problem into N one-electron problems: solving the Schrödinger equation for a single particle is easy. In this case the N -fermion wavefunction is simply a Slater determinant (in order to achieve the required exchange-antisymmetry) of the N lowest-energy solutions of the one-electron Schrödinger equation: see next paragraph.

In general, a Slater determinant constructed, for N identical fermions, from N selected members of a complete set of normalised, orthogonal one-particle functions $\{\psi_1, \psi_2, \dots\}$ is given by

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(x_1) & \psi_j(x_1) & \cdots & \psi_l(x_1) \\ \psi_i(x_2) & \psi_j(x_2) & \cdots & \psi_l(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_i(x_N) & \psi_j(x_N) & \cdots & \psi_l(x_N) \end{vmatrix}.$$

Because of the alternating signs that form part of the definition of a determinant, a Slater determinant is automatically exchange-antisymmetric, e.g. $\Psi(x_1, x_2, x_3 \dots) = -\Psi(x_2, x_1, x_3 \dots)$.

Such a Slater determinant used for identical non-interacting fermions may be thought of as $\mathcal{A}\{\psi_i(x_1)\psi_j(x_2)\cdots\psi_l(x_N)\}$, where \mathcal{A} denotes “antisymmetrise with respect to exchange of particle coordinates, and normalise”. Similarly for identical non-interacting bosons the eigenstates of the Hamiltonian may be thought of as $\mathcal{S}\{\psi_i(x_1)\psi_j(x_2)\cdots\psi_l(x_N)\}$, where \mathcal{S} denotes “symmetrise with respect to exchange of particle coordinates, and normalise”; in this case it’s allowed to have the same ψ_i for more than one electron.

3.3 Hartree-Fock theory

The idea is to approximate the actual many-electron wavefunction by a Slater determinant (as a trial wavefunction in the variational principle), but to choose the functions ψ_1, ψ_2 , etc., so as to minimise the expectation value of the full Hamiltonian (including interaction, i.e. $\lambda = 1$ in the previous subsection), which, according to the variational principle², then provides a good estimate of (and an upper bound on) the ground-state total energy, E_0 . The resulting equations for the ψ_i are known as the Hartree-Fock equations:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + \hat{\Sigma}_{\text{x}}\right)\psi_i(x) = \varepsilon\psi_i(x).$$

These have the form of the one-electron Schrödinger equation, but with the actual potential due to the nuclei v_{ext} replaced with an *effective potential* which further includes

- the Hartree potential which is the electrostatic potential due to the average charge density of all the electrons:

$$v_{\text{H}}(x) = \int \sum_{j=1}^N |\psi_j(x')|^2 u(|x - x'|) dx'$$

where u is the Coulomb repulsion $e^2/4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|$;

- the non-local potential known as the “exchange operator”:

$$\hat{\Sigma}_{\text{x}}\psi_i(x) = -\int \sum_{j=1}^N \psi_j(x)\psi_j^*(x')\delta_{\sigma_i,\sigma_j}u(|x - x'|)\psi_i(x')dx';$$

where the $\delta_{\sigma_i,\sigma_j}$ restricts the sum to electrons i and j with the same spin orientation.

The Hartree-Fock equations need to be solved self-consistently, for the N lowest wavefunctions and eigenvalues, which are then reinserted into the density expression (for the Hartree potential) and the Fock operator (for the exchange operator), and this cycle is repeated until self-consistency is reached in the wavefunctions.

3.4 Density-functional theory

Hohenberg-Kohn theorem: There exists a universal functional $F[n]$ such that, when $E[n] = F[n] + \int n(\mathbf{r})v_{\text{ext}}(\mathbf{r})d^3r$ is minimised with respect to variations in n , the value of E is the ground-state energy E_0 , and this occurs at the density function $n_0(\mathbf{r})$, the exact ground-state electron density for external potential $v_{\text{ext}}(\mathbf{r})$.

²Variational principle: $\langle \Psi_{\text{T}}|\hat{H}|\Psi_{\text{T}}\rangle - E_0 \geq 0$, where Ψ_{T} is any normalised trial wavefunction (exchange-antisymmetric in the case of identical fermions), and the left-hand side is zero plus terms of *second* order in the error in Ψ_{T} , so that a rather rough estimate, Ψ_{T} , can give a rather accurate estimate of E_0 .

Using this idea, Kohn and Sham showed that this minimisation could be performed by solving the **Kohn-Sham equations** self-consistently, in a similar way to the Hartree-Fock equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}} \right) \psi_i(x) = \varepsilon \psi_i(x).$$

where v_{H} has the same definition as in Hartree-Fock theory, and the exchange-[and]-correlation potential $v_{\text{xc}}(\mathbf{r})$ is a functional of the electron density that needs to be approximated.

The usual approximations are the local density approximation (which assumes each point in space to be part of a homogeneous electron gas) and the generalised gradient approximation (which takes some account of the gradient of the density as well as its local value). They often work pretty well for ground-state properties of the system, but they are not perfect.

4 Second Quantisation

4.1 Creation and annihilation operators

In second quantisation for a system of identical **bosons**, the creation and annihilation operators \hat{a}_k^\dagger and \hat{a}_k are defined in terms of their effects on a normalised many-boson wavefunction formed from exchange-symmetrised products of members of a basis set $\{\phi_1, \phi_2, \phi_3, \dots\}$ of normalised, orthogonal one-particle functions:

$$\begin{aligned} \hat{a}_k^\dagger |n_1, n_2, n_3, \dots, n_k, \dots\rangle &= \sqrt{n_k + 1} |n_1, n_2, n_3, \dots, n_k + 1, \dots\rangle \\ \hat{a}_k |n_1, n_2, n_3, \dots, n_k, \dots\rangle &= \sqrt{n_k} |n_1, n_2, n_3, \dots, n_k - 1, \dots\rangle, \end{aligned}$$

where n_i is the number of particles in state i . \hat{a}_k^\dagger adds a particle to the system, and \hat{a}_k annihilates a particle.

In second quantisation for a system of identical **fermions**, the wavefunction used for the definition $|n_1, n_2, n_3, \dots, n_k, \dots\rangle$ is an normalised exchange-*antisymmetrised* sum of products of the ψ_i , i.e. a Slater determinant of the form given in the previous section, and (for the wavefunction to be non-zero) the n_k are zero or one; \hat{a}_k^\dagger adds a particle to the system by creating a new column ϕ_k as the left-most column (and adding the extra row and changing the normalisation factor to $1/\sqrt{(N+1)!}$), and \hat{a}_k does the reverse. (If \hat{a}_k^\dagger operates on a state in which a particle is already in state k , or \hat{a}_k operates on a state in which no particle is in state k , the value 0 results.)

For bosons we derived the commutation relations $[\hat{a}_k^\dagger, \hat{a}_l^\dagger] = [\hat{a}_k, \hat{a}_l] = 0$; $[\hat{a}_k, \hat{a}_l^\dagger] = \delta_{kl}$,

and for fermions the anticommutation relations $\{\hat{a}_k^\dagger, \hat{a}_l^\dagger\} = \{\hat{a}_k, \hat{a}_l\} = 0$; $\{\hat{a}_k, \hat{a}_l^\dagger\} = \delta_{kl}$.

For both bosons and fermions $[\hat{a}_j, \hat{a}_k^\dagger \hat{a}_l] = \hat{a}_l \delta_{kj}$ and $[\hat{a}_j, \hat{a}_q^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_t] = \hat{a}_r^\dagger \hat{a}_s \hat{a}_t \delta_{qj} + \hat{a}_q^\dagger \hat{a}_t \hat{a}_s \delta_{rj}$.

4.2 Creation and annihilation field operators

A particular set of annihilation and creation operators $\hat{\psi}_\sigma^\dagger(\mathbf{r})$ and $\hat{\psi}_\sigma(\mathbf{r})$ that create and destroy particles **at point** \mathbf{r} with spin σ . The Hamiltonian can be written in terms of any chosen set of annihilation and creation operators, but the field operators are especially convenient because of their focus on position.

4.3 Heisenberg picture

If $\hat{U}(t)$ is the time-evolution operator that, through the time-dependent Schrödinger equation, propagates the wavefunction from time 0 to time t , i.e. $\hat{U}(t)\psi(0) = \psi(t)$, can define for an oper-

ator \hat{A} the corresponding operator in the Heisenberg picture³ $\hat{A}_H(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t)$, moving all the time-dependence out of the wavefunction and into the operators. The equation of motion of \hat{A}_H is

$$\frac{d}{dt}\hat{A}_H(t) = \frac{1}{i\hbar}[\hat{A}_H(t), \hat{H}] + \left(\frac{\partial \hat{A}}{\partial t}\right)_H$$

(the last term entering only if \hat{A} happens to have built-in time-dependence) which can be used to determine the equation of motion of the annihilation and creation operators, and in particular in terms of the field operators.

4.4 Uses of second quantisation

In order to formulate *many-body perturbation theory*, the equations of motions just mentioned can be used to determine the equation of motion of the Green's function G (which describes the propagation of an added particle, and is defined in terms of the field operators). This leads to a set of coupled equations which, when solved iteratively, allows G to be calculated to a given order in (e.g.) the particle-particle interaction strength, without explicitly needing to consider many-particle wavefunctions. G is related to experimental quantities of interest, e.g. electron spectroscopy.

In *quantum electrodynamics*, similar field operators represent not the creation and destruction of particles, but the creation and destruction of a quantum of energy in a mode of the electromagnetic field, and field operators correspond to the classical fields \mathbf{E} and \mathbf{B} , or alternatively the potentials \mathbf{A} and Φ . These "field" field operators together with the "particle" field operators appear in the overall Hamiltonian for electromagnetic fields interacting with charged particles (i.e. matter). The electromagnetic field is now properly quantised, and spontaneous emission (of energy from the electron into the EM field) is described, as well as stimulated emission and absorption that were already described when the EM field was treated classically.

³The more familiar wavefunctions and operators are known as the "Schrödinger picture".