

16 What to know in May

16.1 An experimental topic

Quantum Mechanics is our best description of what we observe in experiments, even though we cannot observe the wavefunction.

16.2 The wavefunction and interference

The wavefunction expresses everything we can know about a quantum system, and nothing we can't know. A wavefunction cannot be measured, indeed it may not be representable by a real number. On "measurement", which is any process which could in principle be used to determine a particular quantum state, the wavefunction collapses.

16.3 Basis functions

Any quantum state can be expanded in a complete set of basis functions. The choice of basis set has no physical meaning.

16.4 Expectation value

The expectation value is the predicted mean value of the result of an experiment for a system in a given quantum state. This mean value may not correspond to any of the quantised states of the system if it is not in an eigenstate of the operator whose expectation value is sought.

16.5 Integrals

The most important property of a matrix element is whether it is zero. This determines whether something can happen or not.

16.6 Curvature

The kinetic energy is related to the curvature of a wave. Thus ground states tend to have smooth wavefunctions and no nodes.

16.7 Time independent Perturbation Theory

For the energy, to first order, you can assume that the wavefunction is unchanged and evaluate the energy shift from the matrix element

$$\Delta E_0 \approx \langle n_0 | \hat{V} | n_0 \rangle \equiv V_{00}$$

For the wavefunctions, the amount of other unperturbed wavefunction mixed in depends on the matrix element between them, and their energy difference.

$$|\phi_0\rangle = |n_0\rangle + \sum_{k \neq 0} \frac{\langle n_k | \hat{V} | n_0 \rangle}{(E_0 - E_k)} |n_k\rangle \equiv |n_0\rangle + \sum_{k \neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

For the energy, to second order, we consider mixing of the wavefunctions:

$$\Delta E_0 = 0 + \sum_{i=1,\infty} \langle n_i | \hat{V} | n_0 \rangle \frac{V_{0i}}{(E_0 - E_i)} = \sum_{i=1,\infty} \frac{|V_{i0}|^2}{(E_0 - E_i)}$$

16.8 Degenerate Perturbation Theory

The perturbed wavefunction is a linear combination of the unperturbed, degenerate states. Calculate eigenstates and eigenvalues from the matrix:

$$\begin{vmatrix} V_{11} - \Delta E_j & V_{12} & \dots & V_{1N} \\ V_{21} & V_{22} - \Delta E_j & \dots & V_{2N} \\ \dots & \dots & \dots & \dots \\ V_{N1} & V_{N2} & \dots & V_{NN} - \Delta E_j \end{vmatrix} = 0$$

With every degeneracy there is an associated symmetry and conservation law.

16.9 Time-dependence

Wavefunctions oscillate in time as $\exp(iEt/\hbar)$ but intensities do not $e^{-iEt/\hbar}e^{iEt/\hbar} = 1$.

16.10 Time-dependent Perturbation Theory

If a system starts in state $|k\rangle$, ($c_m(t) = 0$) the probability that it will shift to state $|k\rangle$ in time t depends on the matrix element

$$c_m(t) = (i\hbar)^{-1} \int_0^t V_{mk} \exp(i\omega_{mk}t) dt$$

For a harmonic perturbation we get a resonance when the perturbing frequency matches the energy difference between the states m and k :

$$|c_m(t)|^2 = \frac{V_{mk}^2 \sin^2[(\omega_{mk} - \omega)t/2]}{\hbar^2(\omega_{mk} - \omega)^2} = \frac{4}{\hbar^2} V_{mk}^2 f(t, \omega_{mk} - \omega)$$

Energy is extracted from the perturbing potential.

If the transition is to a group of near-degenerate states, The transition rate depends on the square of the matrix element, and the density of states, as given by Fermi's Golden rule:

$$R = \frac{2\pi}{\hbar} [|V_{mk}|^2 g(E_m)]_{E_m=E_k}$$

16.11 Variational Principle

A surprisingly good estimate of the ground state energy comes from minimising the expectation value of the energy for an arbitrary, normalised trial wavefunction $\phi(a_n)$.

$$E[a_n] \approx \text{Min}_{a_n} \left(\frac{\langle \phi(a_n) | \hat{H} | \phi(a_n) \rangle}{\langle \phi(a_n) | \phi(a_n) \rangle} \right)$$

Excited states can also be found using trial wavefunctions orthogonal to the ground state.

16.12 Indistinguishable Particles

Quantum mechanical intensities cannot depend on labels on indistinguishable particles. Thus wavefunctions must be either symmetric (bosons) or antisymmetric (fermions) with respect to exchange of any such labels. Appropriate wavefunctions are “Slater determinants” of matrices.

16.13 Binding

The Born-Oppenheimer decouples dynamics of light particles from those of heavy particles, by assuming the light particles are always in the ground state. Atoms and molecules are held together by mixing of atomic wavefunctions into symmetric *gerade* bound states.

16.14 Exchange

Much of the bonding comes from *exchange* integrals - interference between an electrons on different atoms. When two particles are indistinguishable, the wavefunction must be (anti)symmetric, so is usually a sum of two terms. Since measurable quantities (intensities, matrix element) involve the wavefunction times itself, this gives interference terms: exchange.

16.15 Many-Fermions

Because of difficulties with correlation, exact calculations for many Fermion problems are not possible. Self-consistent field theory is the only practical way to proceed, and this requires numerical calculation to sampling possible distributions of particles. This type of calculation is the heaviest user of supercomputing in physics (alongside weather/climate models). The density functional theory, which describes correlation as a parameterised function of the electron density, is now the central method in materials physics and is accurate to a few percent.

16.16 Scattering

Describing scattering involves solving the Schrodinger equation for an incoming plane wave and outgoing spherical wave.

16.17 Born Approximation

At high energy, scattering can be treated by perturbation theory. The scattered wave depends on a matrix element which is the Fourier transform of the potential.

$$\langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle = \int \int \int V(\mathbf{r}) \exp(-i\chi \cdot \mathbf{r}) d\tau; \quad \chi \equiv \mathbf{k}' - \mathbf{k}$$

For elastic scattering from a central potential this becomes:

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{(k \sin \frac{\theta}{2})^2 \hbar^4} \left| \int_0^\infty r V(r) \sin(2kr \sin \frac{\theta}{2}) dr \right|^2$$

16.18 Partial Wave Analysis

Low energy scattering is homogeneous: we consider only *s*-waves.

16.19 Hidden Variables

Quantum mechanics requires a collapse of a spatially extended wavefunction instantaneously. If it could be used to transport information, this “action at a distance” would conflict with relativity, but nobody has yet done so.

16.20 Relativistic Quantum Mechanics

The Schroedinger equation is non-relativistic. The Klein Gordon equation, the natural generalization to $E^2 = p^2c^2 + m^2c^4$, gives “free particle” solutions with negative energy and negative probability. The Dirac Equation, another generalisation, can only be solved for a four-component wavefunction, which represents spin-half and antimatter.

16.21 Measurement

A measurement is an interaction between the quantum system and the rest of the universe which collapses the system into an eigenstate of the quantity being measured