ph235 Quantum Revision Sheet

In **classical mechanics**, positions and energies of objects can be measured accurately and future positions and energies can be predicted accurately from those observations.

Systems of atomic or sub-atomic size ("quantum systems") cannot be treated in this way: In **quantum mechanics**, positions and energies cannot both be measured independently (**uncertainty principle**). A quantum system, when left alone, can be in any state (*i.e.* have any position and energy) just as in the classical case. However, any measurment will throw it into one of a number of possible distinct states (the **eigenstates**). Any state can be described as a **linear combination** of these eigenstates, with the linear coefficients representing the **probabilities** of measuring each of the eigenstates. When we do a measurement, we pick one of the eigenstates that make up the mixed state the system was in before the measurement.

The possible eigenstates and their corresponding eigenvalues are determined by solving the Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

for the particular system of interest. The **Hamilton operator** $\hat{H}$ describes the kinetic and potential energies; it is applied to the **wave function** Ψ. The equals sign means that we are looking only for those functions for which applying the operator results simply in a multiple of the function itself.

> Mathematical reminder: If we have an operator
>
> $$\hat{A} = x\frac{\mathrm{d}}{\mathrm{d}x}$$
>
> (*i.e.* "take derivative with respect to x, then multiply by x") and an eigenvalue equation
>
> $$\hat{A}f(x) = cf(x) \qquad ,$$
>
> then the function $f(x) = x^2$ is an eigenfunction because
>
> $$\hat{A}f(x) = \hat{A}x^2 = x\frac{\mathrm{d}}{\mathrm{d}x}x^2 = x \cdot 2x = 2x^2 \qquad .$$
>
> Thus the eigenvalue is $c = 2$. There are also other eigenfunctions which solve the equation. These will generally produce different eigenvalues.

By solving the Schrödinger equation, we obtain the eigenvalues E that correspond to the eigenfunctions (or eigenstates) Ψ. By checking the units, you can verify that the eigenvalues are the energies of the eigenstates. Therefore the positional information must be in the eigenfunctions: The **probability** of finding the particle studied in a particular volume element is given by the complex square of the eigenfunction $\Psi^*\Psi$.

Quantum mechanics has a small number of **fundamental concepts** which can be solved analytically. For each of them, a Hamilton operator (consisting of a **kinetic**

energy operator and a **potential**) and a suitable **reference frame** reflecting the geometry of the system have to be found in order to establish the specific Schrödinger equation. Then **boundary conditions** are needed to solve the equation.

> Among the fundamental systems discussed in (both parts of) the lecture are:
> - the free particle
> - the particle in an infinite well (or infinite box)
> - the particle in a finite well
> - the particle in a Coulomb well
> - the harmonic oscillator
> - the rigid rotor
> - the hydrogen-like atom
>
> *Fill in the table overleaf to remind yourself of the different reference frames, potentials, kinetic energy operators, boundary conditions, and resulting eigenfunctions and eigenvalues. It is also a good idea to sketch the potentials and geometries of the systems.*

Real systems are approximated by combining some of these concepts. Most of the work in applied quantum mechanics is choosing the right ingredients relevant to a particular real physical system such as a molecule or an electron in a solid. It is not necessary to solve the Schrödinger equation for these real systems because a linear combination of the solutions obtained for the *relevant* fundamental concepts will usually do.

In addition to this pick-and-mix approach, the systems can often be simplified by exploiting symmetries, *e.g.* by using the **reduced mass** located at the centre of gravity of two particles instead of dealing with both particles separately. In the hydrogen-like atom, if all states with the same quantum number n are occupied, this results in a symmetrical, spherical, electron cloud. This symmetry is exploited by considering the nucleus and the spherical electron shells as a single atom core with an effective charge $Z_{eff}e$ ("**shielding**").

As an example of a real system, we have considered a simple binary **molecule** such as oxygen, O_2. We can treat each of the two oxygen atoms as a hydrogen-like atom, with the $n=1$ electrons incorporated into the atom core. Now, each of the two hydrogen-like atoms comes with its own spherical reference frame. The molecule is most stable if the electron density between the two cores is maximised. Therefore, the eigenstates of each of the atoms are mixed so that the probability cloud of the electrons is maximised between the cores ("**hybridisation**"). This mixing process means that a wave function is found, again by linear combination of the eigenstates ("linear combination of atomic orbitals, **LCAO**"), which has a maximum in the desired place. In order to explain the molecular spectrum of oxygen, we also need to take into account that the molecule can rotate around an axis perpendicular to the bond, and that the bond itself is not

rigid but more like a spring with two masses atached. This behaviour can be added to the model by mixing in the solutions of the rigd rotor and the harmonic oscillator. Thus, to approximate an oxygen molecule, four fundamental systems are combined: two hydrogen-like atoms, a rigid rotor, and a symmetric harmonic oscillator.

Similarly, a crystalline solid can be approximated by an infinite number of identical Coulomb wells and harmonic oscillators. The LCAO argument leads to dense energy bands rather than individual energy levels, because a "molecular" state is generated for each atomic state mixed in. As far as the electronic properties of a solid are concerned, it is sufficient to deal just with the energy bands thus created. The atom cores can be neglected because the outer electrons are located in the delocalised bands above the potentials of each individual core.

concept	coordinates	potential	kin. en. op.	boundary cond.	wave func.	eigenvalues
free particle			$-\frac{\hbar^2}{2m}\hat{\nabla}^2$	none		
particle in infinite well	1D linear (z)		$-\frac{\hbar^2}{2m}\hat{\nabla}^2$		$B\sin(\frac{2\pi a}{h} \cdot \sqrt{2mE})$	
particle in finite well		$0\ (0 < z < a)$; V_0 (otherwise)		$\Psi(0)$ steady; $\Psi(a)$ steady		
particle in Coulomb well		$V(r) = -\frac{qQ}{4\pi\epsilon_0 r}$				
harmonic oscillator	1D linear (origin: centre of gravity)				$\sum_{i=0}^{n/2} c_{2i}z^{2i} \cdot \exp\left(-\frac{\pi\nu z^2 m}{\hbar}\right)$	
rigid rotor		0	$-\frac{\hbar^2}{2\mu}\hat{\nabla}^2$			$E_J = \frac{\hbar^2}{2I}J(J+1)$
hydrogen-like atom	spherical (r,θ,φ)			$\Psi(r \to \infty) = 0$; $\Psi(\varphi = 0)$ $= \Psi(\varphi = 2\pi)$		$E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 h^2 n^2}$