

Quantum Mechanics of Atoms & Molecules - A Summary

1 Preliminaries

This will assume a lot of knowledge of previous QM courses: this document will not be that extensive!

The expectation value of an operator, in a given state:

$$\langle \hat{A} \rangle = \int d^3r \psi_k^* \hat{A} \psi_k = \langle k | \hat{A} | k \rangle \quad (1.1)$$

The transpose of an operator: think that it acts to the left, as opposed to the usual right:

$$\psi \hat{A} \phi = \phi \tilde{A} \psi$$

Then the Hermitian conjugate of an operator, is the complex conjugate of the transpose:

$$\hat{A}^\dagger \equiv (\tilde{A})^* \quad (1.2)$$

If $A |k\rangle = k |k\rangle$, then the representation of some other operator B , in the basis of eigenstates of A is given by:

$$B_{kk'} = \langle k | B | k' \rangle$$

2 Harmonic Oscillator

We have the standard Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} m \omega^2 x^2$$

We define the *destruction operator*:

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \frac{\hat{p}}{\sqrt{2m\omega\hbar}} \quad (2.1)$$

The *creation operator* is the Hermitian conjugate of the above: \hat{a}^\dagger .

From these definitions, we are able to construct the Hamiltonian in terms of a and a^\dagger (I shall now suppress hats on operators, unless necessary):

$$\hat{H} = \hbar\omega \left(\frac{1}{2} + a^\dagger a \right)$$

We have the following commutator:

$$\left[a, a^\dagger \right] = 1 \quad (2.2)$$

We have the action of both operators on some state:

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad a |n\rangle = \sqrt{n} |n-1\rangle \quad (2.3)$$

So, we have the action of the creation operator, n times, on the zero-state:

$$(a^\dagger)^n |0\rangle = \sqrt{n!} |n\rangle$$

3 Angular Momentum

The states are $|\ell, m\rangle \rightarrow Y_{\ell m}(\theta, \phi)$.

Here I shall just state a load of commutators & relations:

$$L^2 |\ell, m\rangle = \hbar^2 \ell(\ell + 1) |\ell, m\rangle \quad (3.1)$$

$$L_z |\ell, m\rangle = \hbar m |\ell, m\rangle \quad (3.2)$$

$$L^\pm \equiv L_x \pm iL_y \quad (3.3)$$

$$L^\pm |\ell, m\rangle = \hbar \sqrt{\ell(\ell + 1) - m(m \pm 1)} |\ell, m \pm 1\rangle \quad (3.4)$$

$$[L^2, L_z] = 0 \quad (3.5)$$

$$[L_z, L^\pm] = \pm \hbar L^\pm \quad (3.6)$$

$$[L^+, L^-] = 2\hbar L_z \quad (3.7)$$

4 Independent Particle Approximation

For an N particle system, the Hamiltonian will be given by:

$$H = \sum_{i=1}^N H_i + V$$

Where \hat{H}_i are the single-particle Hamiltonians, and the interaction potential is V . For example, in Lithium, with 3 electrons, the interaction potential is:

$$V = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

The independent particle approximation is to ignore V completely.

So, the total wavefunction can be expressed as a product of the single-particle wavefunctions:

$$\psi_k(\mathbf{x}) = \prod_j^N \phi_{kj}(x_j)$$

Then, the single particle Schrodinger equation looks like:

$$H_j \phi_{kj} = E_{kj} \phi_{kj}$$

The total Schrodinger equation looks like:

$$H \psi_k = E_k \psi_k$$

So that the total Hamiltonian and energies are:

$$E_k = \sum_j^N E_{kj} \quad H = \sum_j^N H_j$$

The total wavefunction is a product of spatial wavefunctions & spin:

$$\psi(x_1, \dots, x_N) = \phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\chi(\sigma_1, \dots, \sigma_N) \quad (4.1)$$

Bosons have symmetric overall wavefunctions; and fermions antisymmetric.

If ψ is to be symmetric, then both ϕ, χ must be symmetric (anti).

If ψ is to be antisymmetric, then ϕ must be symm (anti) and χ anti (symm).

4.1 Electron Configuration & Ground States

We have the following:

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10} \quad (4.2)$$

The maximum number of electrons in a given ℓ is obviously given by $2\ell(\ell + 1)$.

The *atomic spectral term* is given by:

$$^{2S+1}L_J \quad (4.3)$$