

Lecture 12 Highlights

Phys 402

We discussed the structure of the periodic table based on the concept of electrons filling Hydrogenic ‘orbitals’ as the nuclear charge is increased. The Pauli exclusion principle prevents double occupation of electron states in an atom. Therefore, every electron added to an atom must have a unique list of quantum numbers $|n, \ell, m_\ell, m_s\rangle$ associated with its state. The electrons fill these orbitals in the order of increasing n that we would expect from the solution of the unperturbed hydrogen atom (since $E_n^0 = -\frac{13.6 \text{ eV } Z^2}{n^2}$, where the nuclear charge of the Hydrogenic atom nucleus is $+Ze^2$). At some point (namely $\text{Ar} \rightarrow \text{K}$) the order is altered, and a state with larger n but smaller ℓ is favored over one with smaller n but larger ℓ . The reason for this is the fact that $\ell = 0$ classical orbits involve the electron spending more time inside the screening cloud surrounding the nucleus created by the core electrons. In addition, the larger n but smaller ℓ orbital has a smaller Coulomb overlap with the core electrons, also tending to favor it. This is the same effect mentioned in the last lecture (illustrated [here](#)), and becomes increasingly important for atoms of larger nuclear charge.

We also discussed the formation of a covalent bond, using the hydrogen molecule H_2 as an example. When two hydrogen atoms are brought together and the electron wavefunctions overlap we have to construct a fully anti-symmetrized wavefunction for the molecule. As with He, this involves constructing symmetric and anti-symmetric space wavefunctions, along with symmetric and anti-symmetric spinor wavefunctions. The spinors are again the spin-singlet (anti-symmetric) and spin-triplet states (symmetric). The space wavefunctions specify the nucleus and electron, and have the following form:

$$\Psi_{H_2}^{SA}(1,2;a,b) = \frac{1}{\sqrt{2}} \{ \psi_{100}(1;a)\psi_{100}(2;b) + \psi_{100}(1;b)\psi_{100}(2;a) \} |0\ 0\rangle$$

or

$$\Psi_{H_2}^{AS}(1,2;a,b) = \frac{1}{\sqrt{2}} \{ \psi_{100}(1;a)\psi_{100}(2;b) - \psi_{100}(1;b)\psi_{100}(2;a) \} |1\ m\rangle,$$

with

$$m = +1, \ 0, \ -1$$

(super-scripts “A” and “S” stand for Antisymmetric and Symmetric, respectively). Here $\psi_{100}(1;a)$ means electron 1 is orbiting nucleus a in the $n\ell m = 100$ state. These wavefunctions are overall anti-symmetric upon exchange of all the coordinates of the electrons. (Note that the nuclei do not have overlapping wavefunctions.)

By considering a sketch of the total wavefunction of the space symmetric and space anti-symmetric wavefunctions and corresponding probability densities, one finds that the symmetric space case has higher probability density for finding the two electrons between the nuclei. This has three effects; it screens the nucleus-nucleus repulsive interaction, it increases the electron-nucleus attractive interaction by allowing the electrons to spend time close to both nuclei, however it increases the electron-electron Coulomb repulsion. The net effect is to make the symmetric space wavefunction more energetically favorable.

More quantitatively, one can evaluate the [expectation value](#) of the H_2 molecule Hamiltonian as a function of inter-nuclear distance. This shows that the symmetric space (aka “bonding state”) wavefunction has a bound state of the two hydrogen atoms, except

at very small inter-nuclear distance, while the anti-symmetric space wavefunction (aka “anti-bonding state”) has a positive energy at all inter-nuclear distances.

The [plot](#) of $\langle \mathcal{H}_{H_2}^{GS} \rangle$ vs. inter-nuclear distance R shows a clear minimum at an equilibrium distance R_e . The potential around that point is roughly parabolic, so we can write $\langle \mathcal{H}_{H_2}^{GS} \rangle(R) \approx -V_0 + \frac{1}{2} k (R - R_e)^2 + \dots$. We can treat small vibrations of the molecule from equilibrium as a one-dimensional quantum harmonic oscillator. In the case of the KCl molecule, one has $V_0 = 4.42 \text{ eV}$ and $\hbar\omega = 0.0346 \text{ eV}$, which comes from the curvature of the potential energy at the bottom of the well and the reduced mass of the KCl molecule. The vibrational energy levels are given by $E = -V_0 + 0.0346 \text{ eV} (\nu + \frac{1}{2})$, where $\nu = 0, 1, 2, 3, \dots$. Note that there are roughly $\frac{V_0}{\hbar\omega} \sim 100$ vibrational energy levels in the well.

A diatomic molecule can also rotate about an axis that runs through the center of mass (CM) of the molecule. The classical Hamiltonian describes the kinetic energy of rotation as $\mathcal{H} = L^2/2I$, where L is the angular momentum of the molecule in its rotating state, and I is the moment of inertia for the molecule rotation about the chosen axis. The quantum Hamiltonian converts the angular momentum squared into the familiar \hat{L}^2 operator: $\hat{\mathcal{H}} = \hat{L}^2/2I$. The eigenvalues of this operator are just $\ell(\ell + 1)\hbar^2$, hence the energy eigenvalues are $E_\ell = \ell(\ell + 1)\hbar^2/2I$, where the angular momentum quantum number can be $\ell = 0, 1, 2, 3, \dots$. In contrast to the constant-spacing vibrational energy levels, these energy levels become further apart with increasing quantum number. The full ro-vibrational energy level structure is sketched in the last slide of this [link](#).