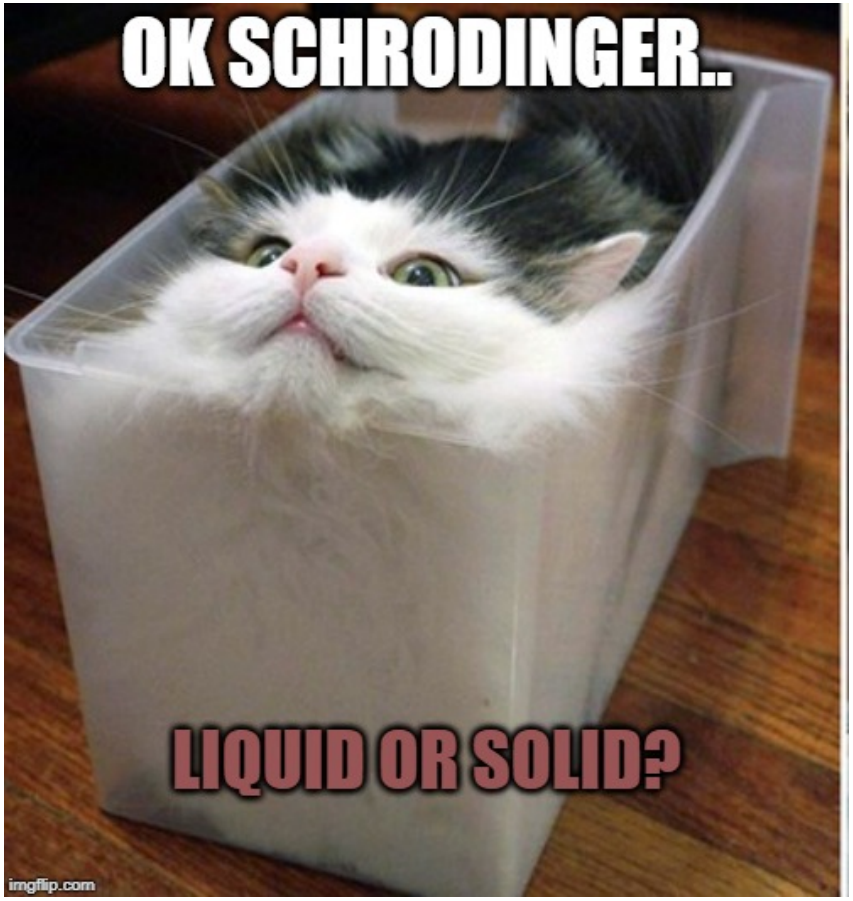
Quantum Mechanics and its Applications PX262 - electrons in atoms and molecules



Opening remarks

- Atoms: H-atom template - language for electronic configurations. Electrons move in potential set up by near static nuclei and the other electrons.
- Molecules: Nuclei move much more slowly than electrons. Electrons 'glue' or bond nuclei together.
- Solids: 10^{24} electrons and nuclei - condensed matter physics.

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- Antisymmetry of many electron wavefunctions,

$$\Psi(x_1, x_2, \cdots, x_i, \cdots, x_j, \cdots) = -\Psi(x_1, x_2, \cdots, x_j, \cdots, x_i, \cdots).$$

- One electron and a symmetric potential, (e.g. H-atom)

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(r)\Psi(\mathbf{r},t)$$

with stationary states

$$\Psi(\mathbf{r},t) = \Phi_{n,l,m}(r,\theta,\phi)u_\sigma e^{-iE_nt/\hbar}$$

where

$$\Phi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

and principal, $n = 1, 2, \cdots$, angular momentum, $l = 0, 1, \cdots, n-1$ and $m = -l, -l+1, \cdots, l$ and spin, $\sigma = \uparrow, \downarrow$, quantum numbers.

- H-atom: $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$, $E_n = -\frac{13.6}{n^2}$ eV.

Atoms.2

- Atom model (Z): Each of the Z e's move in potential from nucleus ($+Ze$ charge) and symmetric cloud of negative charge from other $Z-1$ e's. Net potential is $-\frac{Ze^2}{4\pi\varepsilon_0 r}$ near nucleus and $-\frac{e^2}{4\pi\varepsilon_0 r}$ far away. Lifts l, m degeneracy.
- Electronic configurations: guidelines
  - Fill up Z H-atom states labelled by n, l, m and $\uparrow$ and $\downarrow$ for spin using Pauli Exclusion Principle.
  - Each l sub-shell take up to $2(2l+1)$ electrons.
  - Typical ordering $E_{n0} < E_{n1} < E_{n2} < E_{n3}$ (s,p,d,f) and $E_{32} \approx E_{40}$ (3d = 4s), $E_{42} \approx E_{50}$ (4d = 5s),$E_{52} \approx E_{60}$ (5d = 6s) and $E_{50}, E_{51} < E_{43}$ (5s,5p < 4f).
  - Maximise spin in partly filled shells (Hund's 1st Rule).
  - Examples: B (5), Mo (42), Gd (64)

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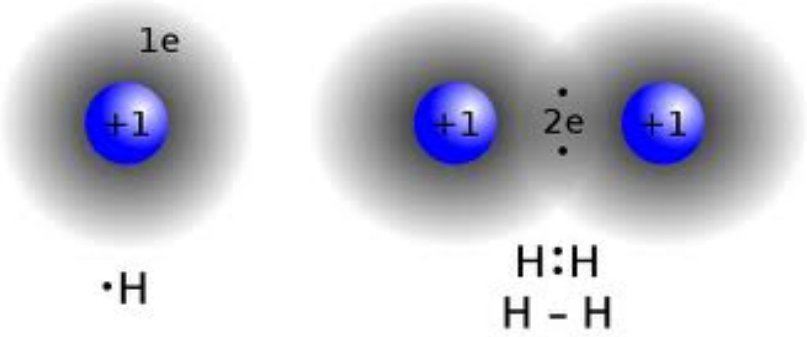
  - Maximise spin in partly filled shells (Hund's 1st Rule).
  - Examples: B (5), Mo (42), Gd (64)
  - B - $1s^2 2s^2 2p^1$ (3);
    Mo - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^4 5s^2$ ([Kr] $4d^4 5s^2$) (6)
    Gd - [Xe] $4f^7 5d^1 6s^2$.

Molecules 1.

- Nuclei slowly oscillating about classical equilibrium positions while electrons move rapidly in near static potential from nuclei and subjected to interactions with each other.
- Nuclei tend to move to positions of minimum electronic and nuclear Coulomb energy. Electrons bond the nuclei.



- Nuclear vibrational energies $(\frac{m_e}{M})^{\frac{1}{2}}$ times smaller than electronic excitation energies. Nuclear rotational energies $\frac{m_e}{M}$ times smaller. eV: 0.01 to 0.1 eV: 0.0001 eV.
- Bonding in molecules. Models from H_2^+ and H_2 insights. Model electronic wave functions ignoring kinetic energy of nuclei.

Molecules 2. Covalent Bonding - H_2 molecule

- First identify all the pieces in the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi\varepsilon_0|\mathbf{R}_A - \mathbf{R}_B|}$$

$$+\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

.

- Good model of 2 electron wavefunction - electrons shared over the two protons:

$$\Psi_{\uparrow\downarrow} = C(|\mathbf{R}_A - \mathbf{R}_B|)(\phi^A_{100}(\mathbf{r}_1)\phi^B_{100}(\mathbf{r}_2) + \phi^A_{100}(\mathbf{r}_2)\phi^B_{100}(\mathbf{r}_1)) \times (\uparrow\downarrow),$$

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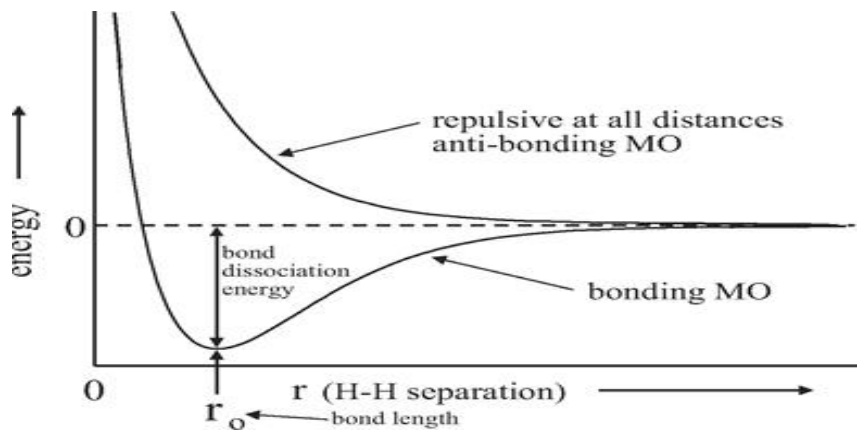

Molecules 3. Ionic Bonding - NaCl molecule

- Electronic configurations from hydrogen-like model.
  Na, $(Z = 11)$, $1s^2\ 2s^2\ 2p^6 3s^1$. 1 loosely bound valence electron.
  Cl, $(Z = 17)$, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$.
- Wavefunction describing all the electrons in this molecule by a model where the Na $3s^1$ electron transfers to fill the Cl 3p shell.
- Both atoms modelled with filled shell configurations. Ionic bond.
- GaAs molecule: ionic or covalent bonding?

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- GaAs molecule: ionic or covalent bonding?
- Ga ($[Ar]3d^{10}\ 4s^2\ 4p^1$) and As ($[Ar]3d^{10}\ 4s^2\ 4p^3$) are either side of Ge in the periodic table. The structure of GaAs might therefore be expected to be similar to that of Ge which would be purely covalent with four electrons involved in the bonding.
- If the bond were fully ionic three electrons would transfer to the As to fill its shell and empty the Ga shell.
- The bonding is best described in terms of a mixture of these two pictures.