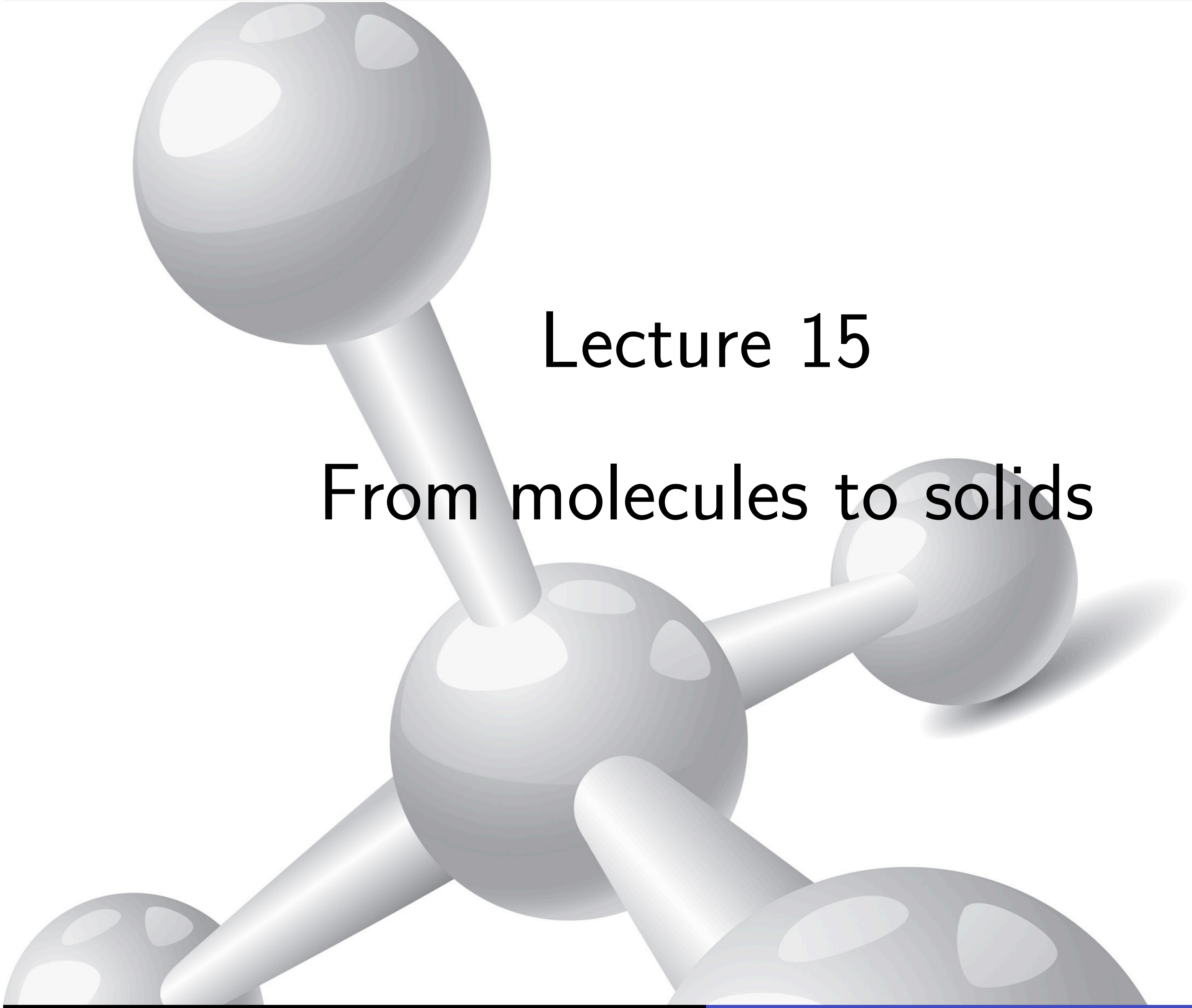
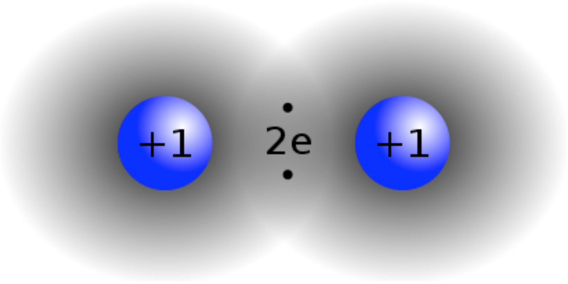


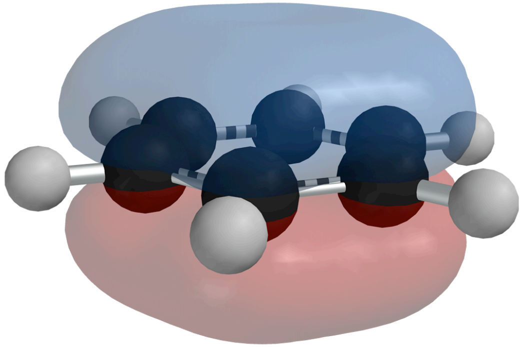
Lecture 15

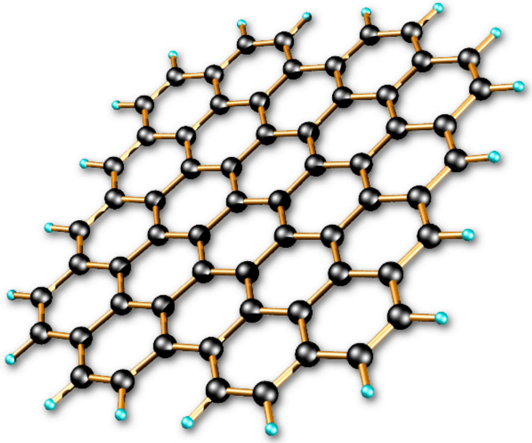
From molecules to solids

Background

- In the last two lectures, we explored quantum mechanics of multi-electron atoms – the subject of atomic physics.
- In this lecture, we will explore how these concepts translate into many-atom systems, from simple molecular structures to solid state.







- Here we will explore H_2^+ and H_2, a simple elemental chain, and a simple two-dimensional crystal (e.g. graphene).

Molecular physics: background

- A molecule consists of electrons moving in the complex potential set up by the charges of the atomic nuclei and other electrons.
- Even in classical mechanics, it would be extremely difficult to solve equations of motion.
- Fortunately, for most purposes, we can treat motion of electrons and nuclei separately, due to their very different masses:

  Since forces that act on nuclei are comparable to those acting on electrons, their momenta are comparable and their velocities are different.
- Therefore, (a) in studying the motion of electrons, we can treat the nuclei as being "nailed down" and
- (b) in studying nuclear motion (vibrations/rotations) we can assume that electrons adjust instantly to changes in molecular conformation:

  basis of **Born-Oppenheimer approximation**.

Born-Oppenheimer approximation

- Wavefunction of a molecule, $\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}, t)$ determined by many-body Schrödinger equation

$$\left[\sum_n \frac{\hat{\mathbf{p}}_n^2}{2m_e} + \sum_N \frac{\hat{\mathbf{p}}_N^2}{2m_N} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})\right] \Psi\psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}, t)$$
$$= \simeq E\, E_k(\{\mathbf{R}_N\})\ \Psi\psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}, t)$$

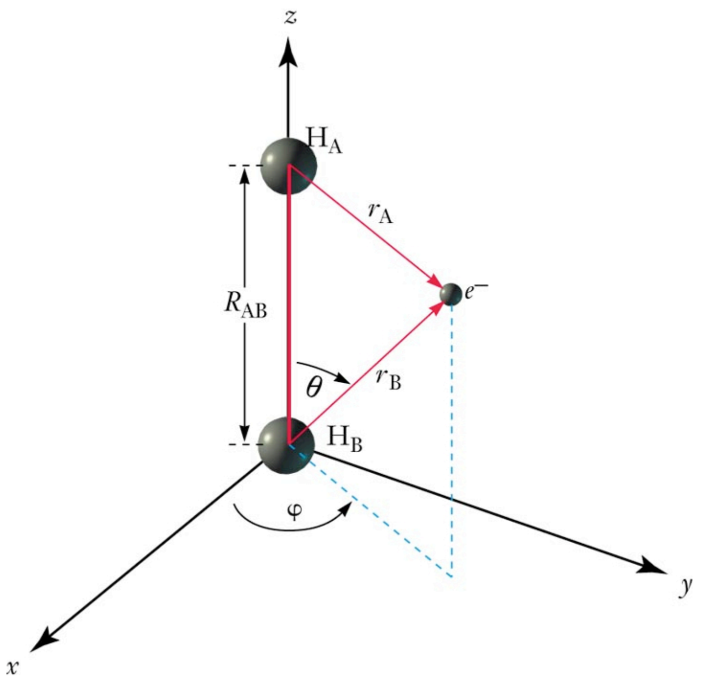
- Since k.e. of nuclei small as compared to electrons, we may drop $\sum_N \frac{\hat{\mathbf{p}}_N^2}{2m_N}$ and focus on electron component of wavefunction:

  Here ψ_k, $k = 0, 1, 2, \cdots$ denote electron wavefunction with nuclei "nailed down" at positions $\mathbf{R}_a, \mathbf{R}_b, \ldots$

- As conformation varied, ground state $E_0(\{\mathbf{R}_N\})$ traces a manifold – **molecular potential energy**; minimum ⇒ equilibrium structure.

The H_2^+ ion

- To apply these ideas, consider simplest molecule, the hydrogen ion H_2^+ – two protons $(\mathbf{R}_a, \mathbf{R}_b)$ and one electron $(\mathbf{r})$.
- H_2^+ is found in abundance in interstellar gas clouds.



- In Born-Oppenheimer approximation, electron Schrödinger equation:

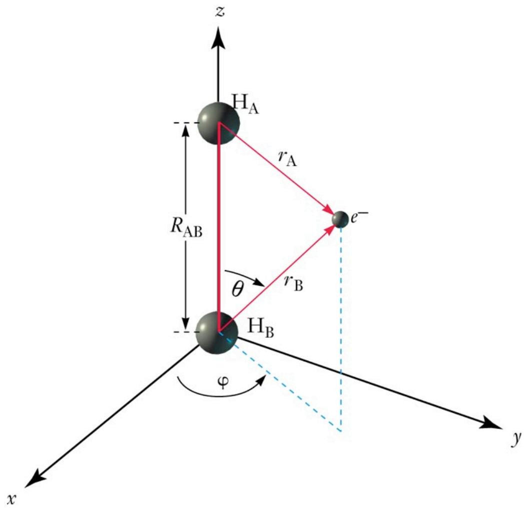
$$\left[\frac{\hat{\mathbf{p}}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{|\mathbf{r}-\mathbf{R}_a|} + \frac{1}{|\mathbf{r}-\mathbf{R}_b|}\right)\right]\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = E\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b)$$

- Although equation can be solved analytically(!), more instructive to look for more general approximation scheme.

The H_2^+ ion

$$\left[\frac{\hat{\mathbf{p}}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{|\mathbf{r}-\mathbf{R}_a|} + \frac{1}{|\mathbf{r}-\mathbf{R}_b|}\right)\right]\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = E\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b)$$

- Since Hamiltonian does not have a "small parameter", we adopt variational approach.
- If electron is close to one proton, expect other to exert only a small influence – here ψ mirrors hydrogen atomic orbital.



- Therefore, in seeking ground state, take trial wavefunction that is linear combination of $1s$ wavefunctions centred on two protons,

$$\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = \alpha\psi_a(\mathbf{r};\mathbf{R}_a) + \beta\psi_b(\mathbf{r};\mathbf{R}_b), \qquad \psi_{a,b}(\mathbf{r}) = \frac{e^{-|\mathbf{r}-\mathbf{R}_{a,b}|/a_0}}{(\pi a_0^3)^{1/2}}$$

where coefficients α and β are taken as real.

The H_2^+ ion

$$\psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = \alpha\psi_a(\mathbf{r};\mathbf{R}_a) + \beta\psi_b(\mathbf{r};\mathbf{R}_b)$$

- Variational ground state energy:

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S}$$

  where $H_{aa} = \langle\psi_a|\hat{H}|\psi_a\rangle = H_{bb}$, and $H_{ab} = \langle\psi_a|\hat{H}|\psi_b\rangle = H_{ba}$.

- Since ψ_a and ψ_b not orthogonal, we have to introduce **overlap integral**, $S = \langle\psi_a|\psi_b\rangle$.
- Since potential is symmetric, wavefunction must be either symmetric or antisymmetric, i.e. $\alpha = \pm\beta$, and

$$\boxed{E_0 \le E = \frac{H_{aa} \pm H_{ab}}{1 \pm S}, \qquad \psi(\mathbf{r};\mathbf{R}_a,\mathbf{R}_b) = \alpha(\psi_a \pm \psi_b)}$$

The H_2^+ ion

$$\boxed{E_0 \leq E = \frac{H_{aa} \pm H_{ab}}{1 \pm S}, \qquad \psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = \alpha(\psi_a \pm \psi_b)}$$

- Two possible wavefunctions for H_2^+ ion,

  $$\psi_g = \frac{\psi_a + \psi_b}{\sqrt{2(1+S)}}, \qquad \psi_u = \frac{\psi_a - \psi_b}{\sqrt{2(1-S)}}$$

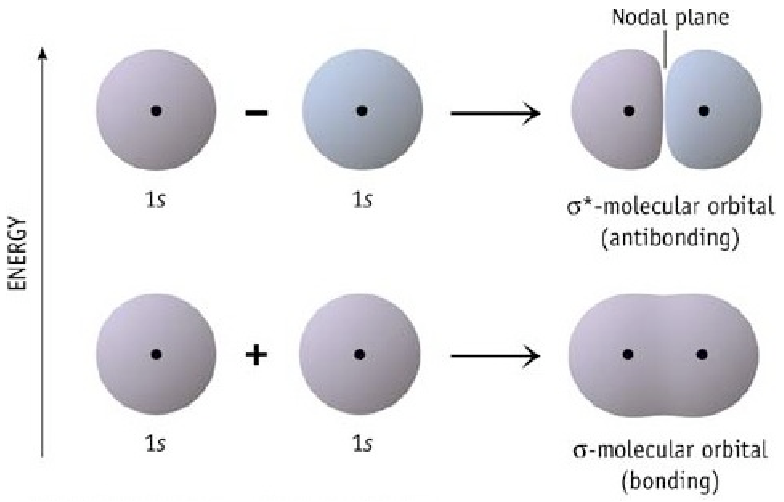
  with energies $E_g = \frac{H_{aa}+H_{ab}}{1+S}$, $E_u = \frac{H_{aa}-H_{ab}}{1-S}$.

- Subscript g (**gerade** – even) used in molecular physics to denote state symmetric under inversion (without exchanging nuclei) The odd (**ungerade**) state denoted by u.

- In chemistry, orthogonal states, ψ_g and ψ_u, are **molecular orbitals** and general methodology is known as the **linear combination of atomic orbitals** (LCAO) approach.

The H_2^+ ion

$$\psi_g = \frac{\psi_a + \psi_b}{\sqrt{2(1+S)}}, \quad \psi_u = \frac{\psi_a - \psi_b}{\sqrt{2(1-S)}}$$

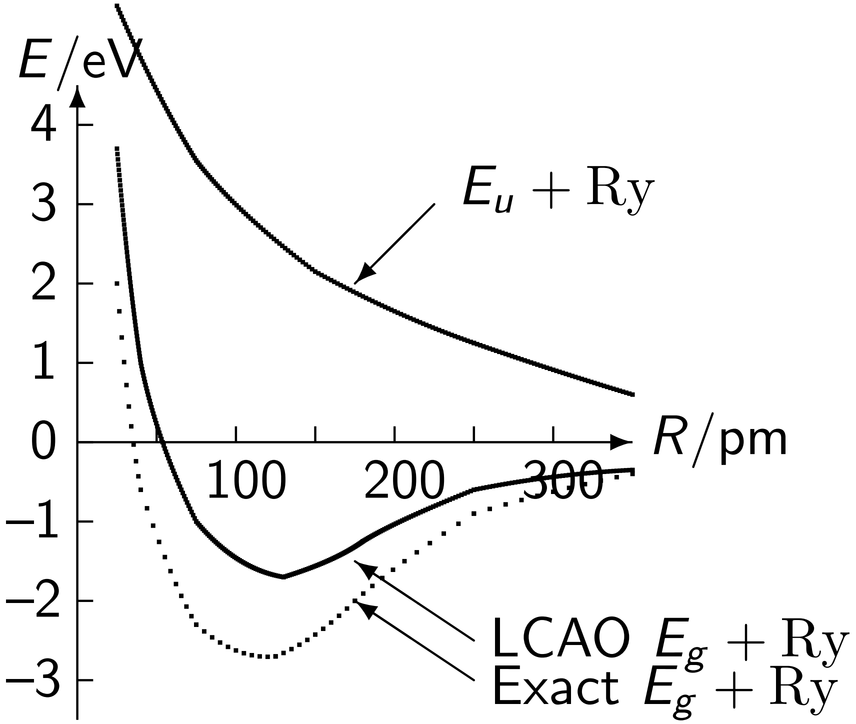


- The state ψ_g has lower energy, while ψ_u represents an excited state of the molecular ion.
- For ψ_g (ψ_u) state, the two atomic wavefunctions interfere constructively (destructively) in region between protons.
- For ψ_g, enhanced electron density in region where electron is attracted by both protons – **screens** protons from each other.

The H_2^+ ion: molecular potential $E(|\mathbf{R}_a - \mathbf{R}_b|)$

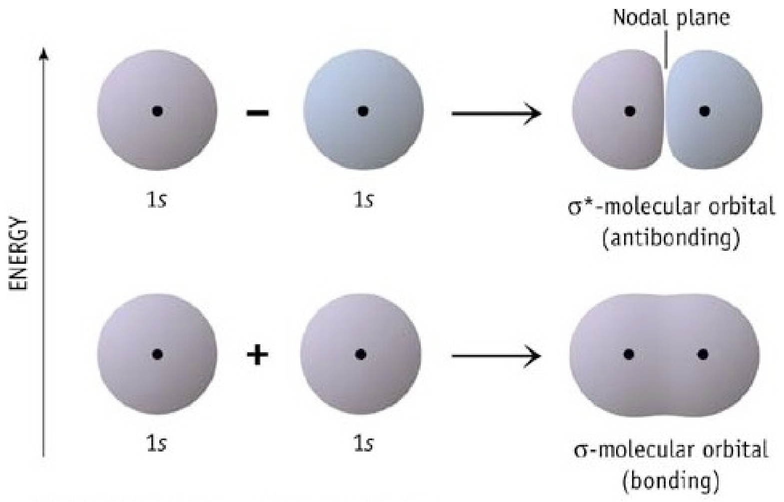
- As expected, variational approximation provides upper limit on ground state energy.

- Since $E_u + \mathrm{Ry}$ does not have a minimum, suggests that odd wavefunction ψ_u does not correspond to bound molecular state.



- To improve approximation, could introduce further orbitals, e.g. at small R wavefunction should approach He^+.

The H_2^+ ion: remarks



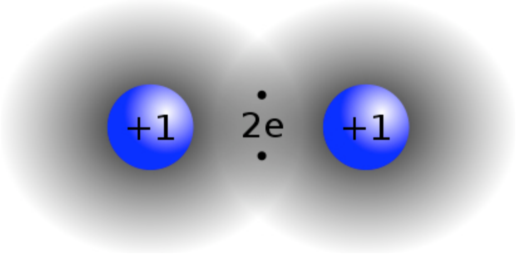
- Although not very accurate, LCAO approximation for ψ_g does exhibit correct features of true **bonding** wavefunction, σ_g:

  (i) it is **even** with respect to inversion;

  (ii) there is **constructive interference** which leads to enhanced probability of finding electron in the region between nuclei.

- ψ_u is characteristic of **anti-bonding** state, σ_u^*.

The H_2 molecule



- At first sight, might expect H_2 is simple extension of H_2^+ ion; but several new features arise. In Born-Oppenheimer approximation, for two electrons $\mathbf{r}_{1,2}$ and two protons, $\mathbf{R}_{a,b}$, $\hat{H} = \hat{H}_0 + \hat{H}_1$ where

$$\boxed{\hat{H}_0 = \sum_{n=1,2} \left[\frac{\hat{\mathbf{p}}_n^2}{2m_e} + V(\mathbf{r}_n) \right], \qquad \hat{H}_1 = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{ab}} \right)}$$

  where $V(\mathbf{r}_n) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{ab}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} \right)$ and $r_{1b} = |\mathbf{r}_1 - \mathbf{R}_b|$, etc., i.e. sum of two H_2^+ ions ($\hat{H}_0$) and an additional term $\hat{H}_1$.

- Since $\langle \frac{1}{r_{12}} \rangle \sim \langle \frac{1}{r_{ab}} \rangle$ can treat $\hat{H}_1$ as a perturbation.

The H_2 molecule

$$\boxed{\hat{H}_0 = \sum_{n=1,2}\left[\frac{\hat{\mathbf{p}}_n^2}{2m_e} + V(\mathbf{r}_n)\right]}$$

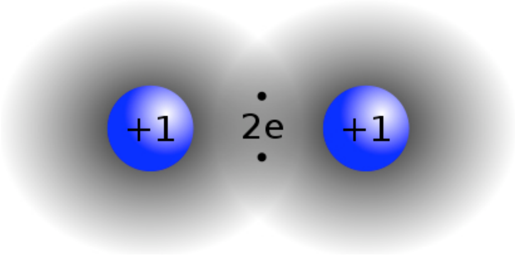
- Neglecting $\hat{H}_1$, there are four ways of filling two orbitals σ_g and σ_u^*,

  $$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_g(\mathbf{r}_1)\psi_{u^*}(\mathbf{r}_2), \quad \psi_{u^*}(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_{u^*}(\mathbf{r}_1)\psi_{u^*}(\mathbf{r}_2)$$

  Of these, expect $\boxed{\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2)}$ to be ground state.
- However, at this stage, we have given no consideration to constraints imposed by particle statistics.
- Since electrons are identical fermions, total wavefunction must be antisymmetric under exchange.
- Taking account of spin degrees of freedom, for both electrons to occupy the bonding σ_g orbital, they must occupy spin singlet state,

  $$\boxed{X_{0,0} = \frac{1}{\sqrt{2}}(\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2))}$$

The H_2 molecule



- If we compute energy of state $\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2)X_{0,0}$ as a function of R, minimum occurs at $R_0 = 85$pm with binding energy of 2.7eV – but true molecule is smaller and more tightly bound.

- Allowing for more variation in atomic orbitals, variable effective charge, etc., gives equilibrium R_0 much closer to experiment, but a binding energy that is still not high enough.

- The reason is that σ_g^2 configuration alone is not a very good representation of the ground state. Why...?

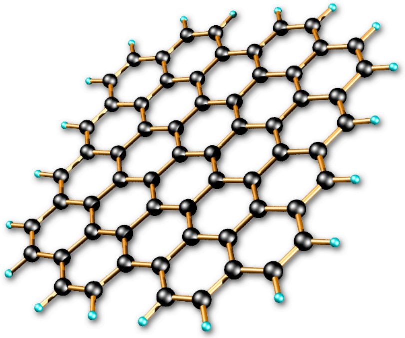
The H_2 molecule

- In the LCAO approximation, σ_g^2 wavefunction has a strange form,

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] \\ + \lambda[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]$$

- First term involves two electrons shared between two hydrogen atoms – a **covalent bond**
- Second term involves both electrons assigned to same atom – an **ionic bond**.
- Since equal coefficients, ionic and covalent contributions are equal $\Rightarrow$ when protons pulled apart, ground state just as likely to consist of H^+ and H^- ion as two neutral atoms! – implausible.
- If we drop ionic part of wavefunction – **valence bonding** approximation – binding energy and nuclear separation improved.
- Including a variational parameter for amplitude of ionic component, find optimal value $\lambda \simeq 1/6 \Rightarrow$ only ca. 3% ionic.

From molecules to solids



- Having established basic principles of molcular structure, we now consider how methodology can be applied to crystalline solids.
- In the Born-Oppenheimer approximation, for **“elemental” solid**,

$$\boxed{\hat{H} = \sum_n \frac{\hat{\mathbf{p}}_n}{2m_e} - \frac{e^2}{4\pi\epsilon_0}\left[\sum_{n,N}\frac{Z}{r_{nN}} - \sum_{m<n}\frac{1}{r_{mn}}\right]}$$

- In the physical system, we would have to take into account the influence of relativistic corrections (viz. spin-orbit interaction).
- To address the properties of such a complex interacting system, we will have to draw upon many of the insights developed previously.

From molecules to solids

- To proceed, helpful to partition electrons into those which are bound to core and those which are unbound. Tightly-bound electrons screen charge leading to a modified nuclear potential, $V_{\rm eff}(\mathbf{r})$.
- Focussing on those electrons which are "free" (**itinerant**),

$$\boxed{\hat{H} \simeq \sum_n \hat{H}_n + \frac{e^2}{4\pi\epsilon_0}\sum_{m<n}\frac{1}{r_{mn}}}$$

  where $\hat{H}_n = \frac{\hat{\mathbf{p}}_n^2}{2m_e} + V_{\rm eff}(\mathbf{r}_n)$ represents "single-particle" Hamiltonian experienced by each electron.

- $\hat{H}_n$ describes motion of an electron in a periodic lattice potential, $V_{\rm eff}(\mathbf{r}) = V_{\rm eff}(\mathbf{r}+\mathbf{R})$ with $\mathbf{R}$ belonging to set of lattice vectors.
- If electrons remain itinerant, they **screen** each other and diminish the effect of electron-electron interaction.

From molecules to solids

- Droping Coulomb interaction between electrons, we can apply molecular orbital theory using variational LCAO scheme: i.e. build trial wavefunction by combining orbital states of single ion, $V_{\mathrm{ion}}(\mathbf{r})$, where $V_{\mathrm{eff}}(\mathbf{r}) = \sum_{\mathbf{R}} V_{\mathrm{ion}}(\mathbf{r})$.
- As with hydrogen molecule, Hamiltonian for individual nuclei, $\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + V_{\mathrm{ion}}(\mathbf{r})$, associated with a set of atomic orbitals, ψ_q, with quantum numbers, q.
- In "**atomic limit**" – when atoms are far-separated, these states mirror simple hydrogenic wavefunctions.
- To find variational ground state of the system, we can then build trial state from a linear combination of these atomic orbitals. Taking only lowest orbital $q = 0$ into account,

$$\boxed{\psi(\mathbf{r}) = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \psi(\mathbf{r} - \mathbf{R})}$$

where, as before, $\alpha_{\mathbf{R}}$ represent set of variational coefficients.

From molecules to solids

- Variational state energy,

$$\boxed{E = \frac{\langle\psi|\hat{H}_0|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} H_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}}$$

where $H_{\mathbf{R}\mathbf{R}'} = \int d^d r\, \psi^*(\mathbf{r}-\mathbf{R})\hat{H}_0\psi(\mathbf{r}-\mathbf{R}')$ denote matrix elements of orbital wavefunction and $S_{\mathbf{R}\mathbf{R}'} = \int d^d r\, \psi^*(\mathbf{r}-\mathbf{R})\psi(\mathbf{r}-\mathbf{R}')$ represent overlap integrals.

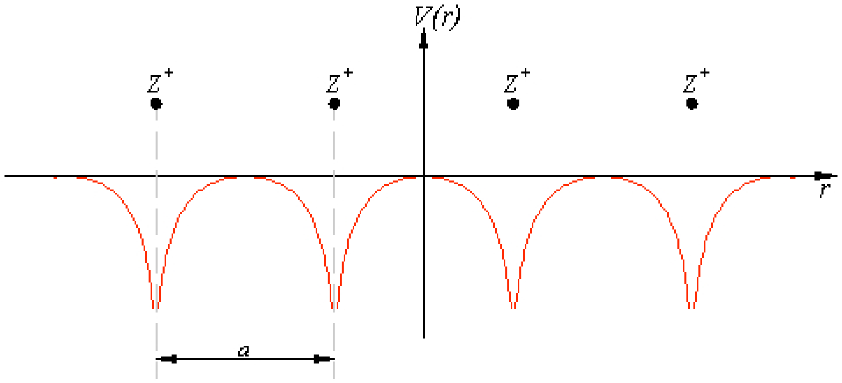
- Minimizing energy with respect to $\alpha^*_{\mathbf{R}}$, obtain **secular equation**,

$$\frac{\delta E}{\delta\alpha^*_{\mathbf{R}}} = \frac{\sum_{\mathbf{R}'} H_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}} - \frac{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} H_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}} E\, \frac{\sum_{\mathbf{R}'} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}}$$

$$\frac{\delta E}{\delta\alpha^*_{\mathbf{R}}} = \frac{\sum_{\mathbf{R}'}\left[H_{\mathbf{R}\mathbf{R}'} - E S_{\mathbf{R}\mathbf{R}'}\right]\alpha_{\mathbf{R}'}}{\sum_{\mathbf{R},\mathbf{R}'}\alpha^*_{\mathbf{R}} S_{\mathbf{R}\mathbf{R}'}\alpha_{\mathbf{R}'}} \overset{!}{=} 0$$

Example: periodic one-dimensional system

$$\boxed{\sum_{\mathbf{R}'}\left[H_{\mathbf{RR}'} - ES_{\mathbf{RR}'}\right]\alpha_{\mathbf{R}'} = 0}$$



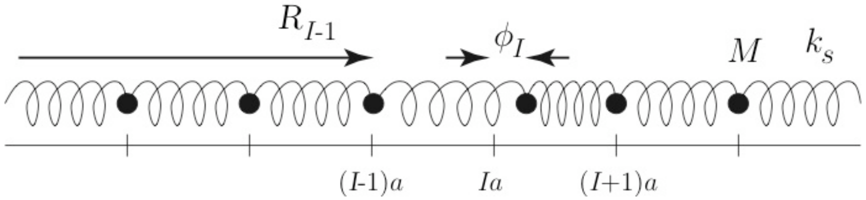
- If atoms are well-separated, overlap integrals and matrix elements decay exponentially with separation.
- Dominant contribution then derives from coupling neighbouring states – **Hückel approximation**. In 1d, secular equation:

$$(\varepsilon - E)\alpha_n - (t + ES)(\alpha_{n+1} + \alpha_{n-1}) = 0, \qquad \text{for each } n$$

where $H_{nn} = \varepsilon$ is atomic orbital energy, $H_{n,n+1} = H_{n+1,n} = -t < 0$ denotes matrix element between neighbouring states, $S_{n,n} = 1$ and $S_{n+1,n} = S_{n+1,n} = S$.

Example: periodic one-dimensional system

$$(\varepsilon - E)\alpha_n - (t + ES)(\alpha_{n+1} + \alpha_{n-1}) = 0$$



- cf. equation of motion of discrete classical N atom "chain":

$$m\ddot{\phi}_n = -k_s(\phi_{n+1} - \phi_n) + k_s(\phi_n - \phi_{n-1}), \qquad \phi_{n+N} = \phi_n$$

with spring constant k_s and masses m. With $\phi_n(t) = e^{i\omega t}\phi_n$,

$$\boxed{(m\omega^2 + 2k_s)\phi_n - k_s(\phi_{n+1} + \phi_{n-1}) = 0}$$

- Normal vibrational modes: $\phi_n = \frac{1}{\sqrt{N}}e^{ikna}$ where $k = \frac{2\pi m}{Na}$ denote N discrete "reciprocal lattice vectors" with $-N/2 < m \leq N/2$.

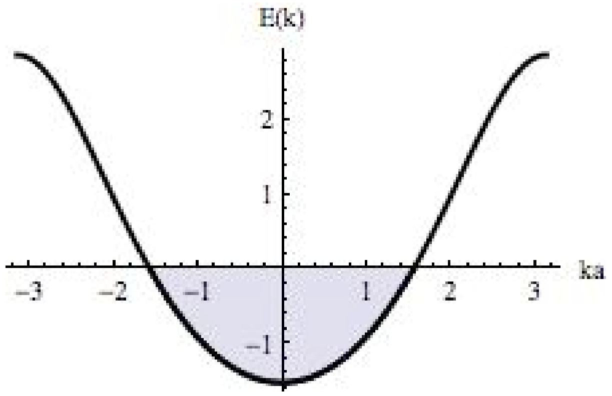
Example: periodic one-dimensional system

$$(\varepsilon - E)\alpha_n - (t + ES)(\alpha_{n+1} + \alpha_{n-1}) = 0$$

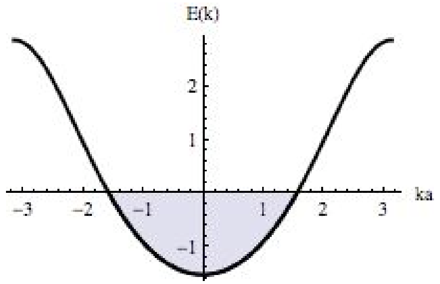
- For N lattice sites and periodic boundary condition, $\alpha_{n+N} = \alpha_n$, solution given by $\alpha_n = \frac{1}{\sqrt{N}} e^{ikna}$,

$$\boxed{E = E_k = \frac{\varepsilon - 2t\cos(ka)}{1 + S\cos(ka)}}$$

i.e. reciprocal lattice vector k parameterizes a **band** of electronic states.

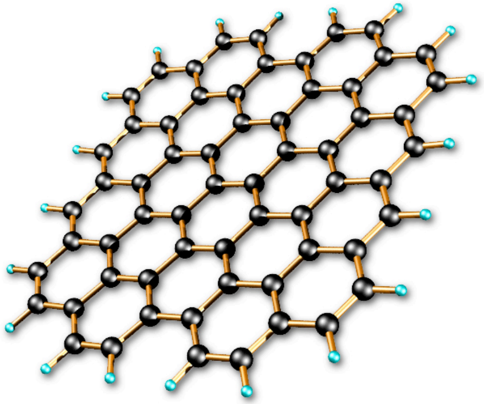


Example: periodic one-dimensional system

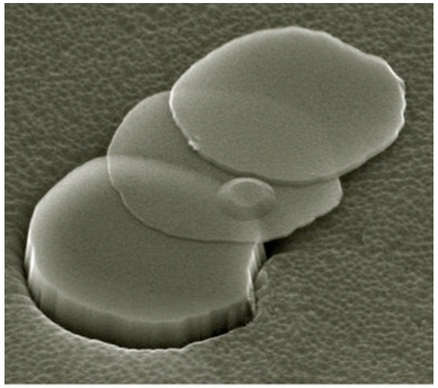


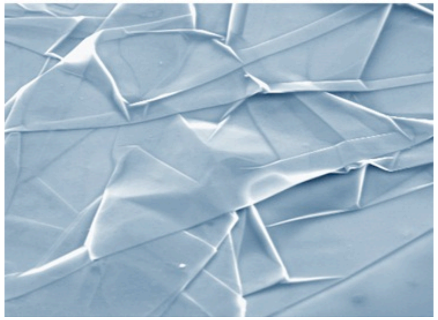
- According to LCAO approximation, for a single electron, lowest energy state predicted to be uniform $\alpha_n = \frac{1}{\sqrt{N}}$ with $E_0 = \frac{\varepsilon - 2t}{1+S}$.
- For more than one electron, we must consider influence of **Pauli exclusion** and **particle indistinguishability**. Since electrons are identical fermions, each state k can host a maximum of two electrons in a spin singlet configuration.
- Lowest energy state obtained by adding electrons sequentially into states of increasing k. If maximum k value – Fermi level – lies within band, excitations cost vanishingly small energy – **metal**. If each atom contributes an even integer number of electrons, Fermi wavevector may lie at a **band gap** – **band insulator**.

Example: graphene



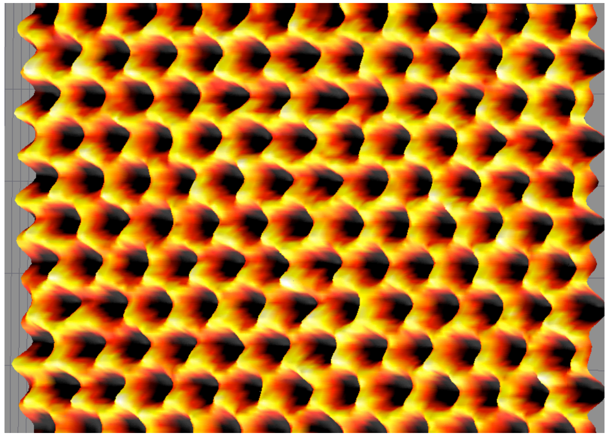
- Recently, much attention has been paid to **graphene**, a single layer of graphite.

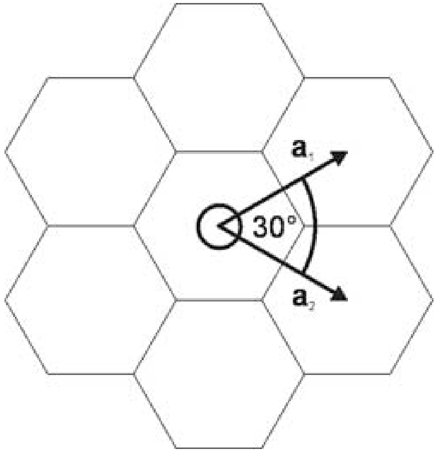




- Flakes of graphene can be prepared by running graphite – a pencil! – over adhesive layer.
- Resulting electron states of single layer compound have been of enormous interest to physicists.
- To understand why, let us implement LCAO technology to explore electronic structure of graphene.

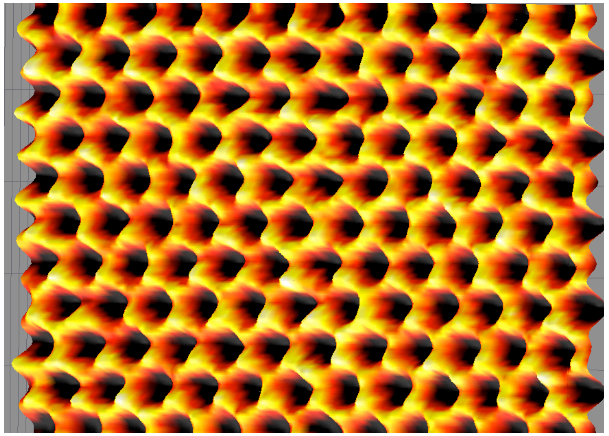
Example: graphene

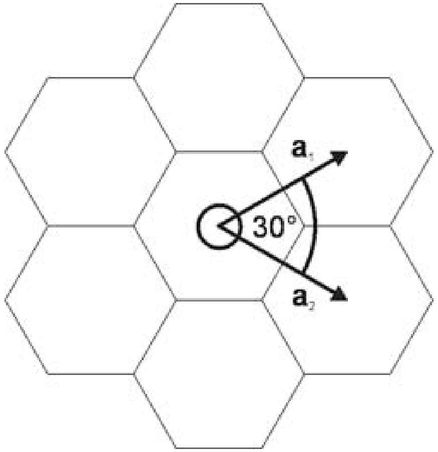




- Graphene forms periodic two-dimensional honeycomb lattice structure with two atoms per unit cell.
- With electron configuration $(1s^2)(2s^2)(2p^2)$, two $1s$ electrons are bound tightly to nucleus.
- $2s$ and $2p$ orbitals **hybridize** into three "sp^2 orbitals" which form covalent σ bonding orbitals and constitute honeycomb lattice.
- Remaining electrons (1/atom), which occupy out-of-plane p_z orbital, is then capable of forming an itinerant band of electron states. It is this band which we now address.

Example: graphene





- Suppose that wavefunction of band involves the basis of p_z orbitals,

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} \left[\alpha_{\mathbf{R}} \psi_1(\mathbf{r} - \mathbf{R}) + \beta_{\mathbf{R}} \psi_2(\mathbf{r} - \mathbf{R})\right]$$

- Taking into account matrix elements involving only nearest neighbours, trial wavefunction translates to secular equation,

$$\begin{aligned}(\varepsilon - E)\alpha_{\mathbf{R}} - (t + ES)(\beta_{\mathbf{R}} + \beta_{\mathbf{R}-\mathbf{a}_1} + \beta_{\mathbf{R}-\mathbf{a}_2}) &= 0 \\ (\varepsilon - E)\beta_{\mathbf{R}} - (t + ES)(\alpha_{\mathbf{R}} + \alpha_{\mathbf{R}+\mathbf{a}_1} + \alpha_{\mathbf{R}+\mathbf{a}_2}) &= 0\end{aligned}$$

  where the primitive lattice vectors $\mathbf{a}_1 = (\sqrt{3}/2, 1/2)a$ and $\mathbf{a}_2 = (\sqrt{3}/2, -1/2)a$, with a the lattice spacing.

Example: graphene

$$(\varepsilon - E)\alpha_{\mathbf{R}} - (t + ES)(\beta_{\mathbf{R}} + \beta_{\mathbf{R}-\mathbf{a}_1} + \beta_{\mathbf{R}-\mathbf{a}_2}) = 0$$
$$(\varepsilon - E)\beta_{\mathbf{R}} - (t + ES)(\alpha_{\mathbf{R}} + \alpha_{\mathbf{R}+\mathbf{a}_1} + \alpha_{\mathbf{R}+\mathbf{a}_2}) = 0$$

- With the plane wave ansatz, $\alpha_{\mathbf{R}} = \frac{\alpha_{\mathbf{k}}}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}}$ and $\beta_{\mathbf{R}} = \frac{\beta_{\mathbf{k}}}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}}$

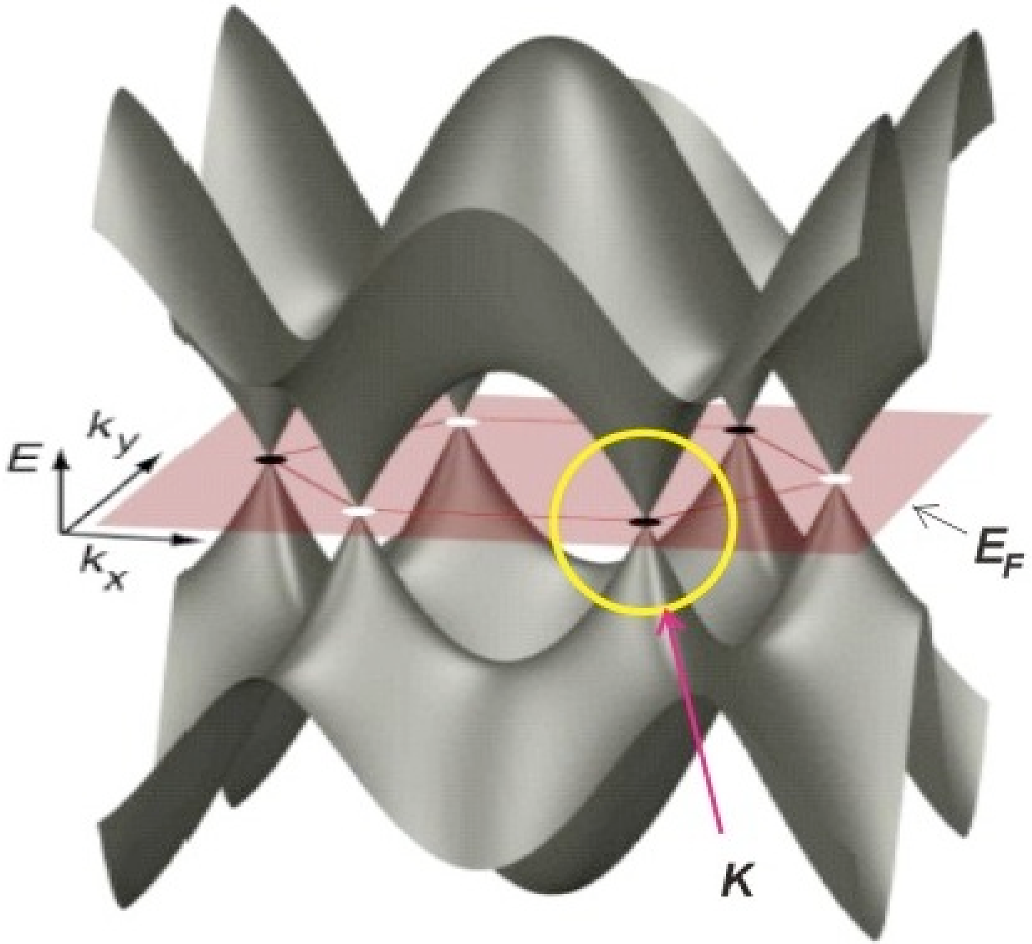
$$(\varepsilon - E)\alpha_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}\beta_{\mathbf{k}} = 0$$
$$(\varepsilon - E)\beta_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}^{*}\alpha_{\mathbf{k}} = 0$$

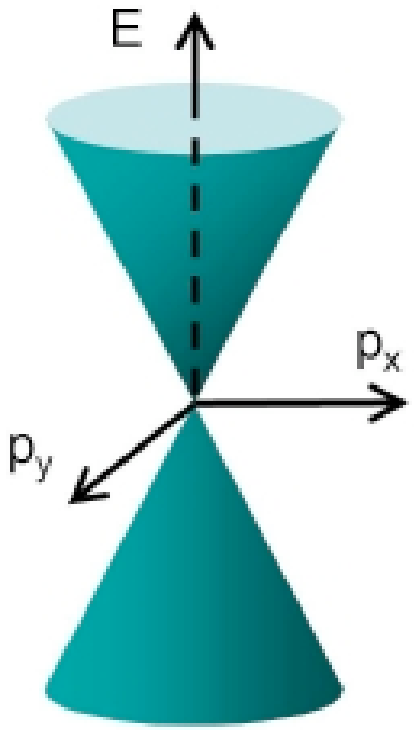
  where $f_{\mathbf{k}} = 1 + 2e^{-i\sqrt{3}k_x a/2}\cos(k_y a/2)$.

- If we neglect overlap integral S (for simplicity),

$$\boxed{E = E_{\mathbf{k}} = \varepsilon \pm |f_{\mathbf{k}}|t}$$

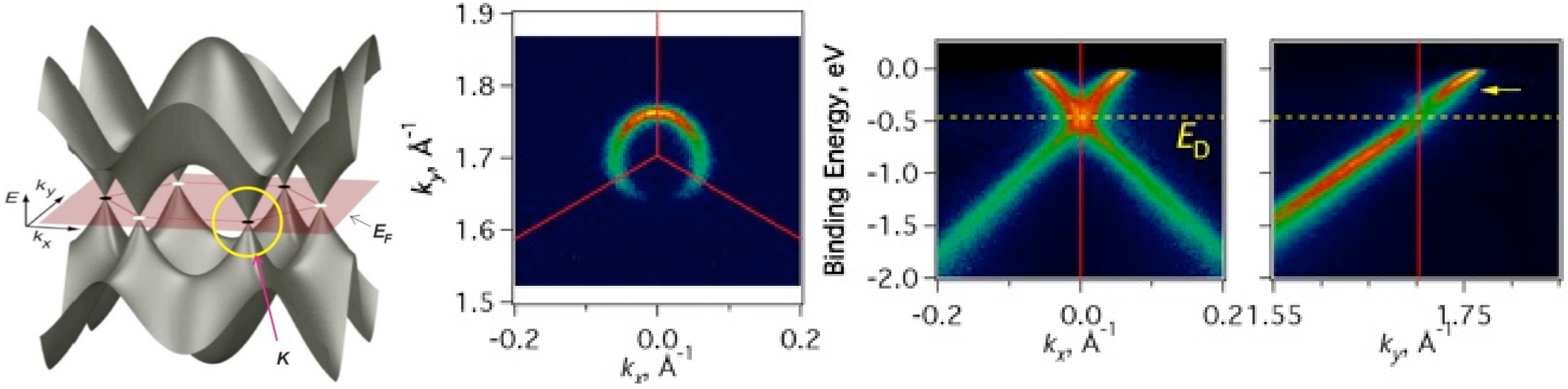
Example: graphene electronic structure





- At "half-filling", where each atom contributes one electron to band, Fermi level lies precisely at centre where dispersion, $E_{\mathbf{k}}$ is point-like.

Example: graphene



- Doping electrons into (or removing electrons from) the system results in (two copies) of a linear dispersion, $E_{\mathbf{k}} \simeq c|\mathbf{k}|$, where c is a constant (velocity).
- Such a linear dispersion relation is the hallmark of a relativistic particle (cf. a photon).
- Although electrons are not moving at relativistic velocities, their properties mirror behaviour of **relativistic particles**.

From molecules to solids

But what about (neglected) electron-electron interactions?

- In principle, we could develop **Hartree-Fock** scheme to address effects on band structure in perturbation theory.
- However, it is a surprising, yet robust, feature of Fermi systems that properties of non-interacting ground state remain qualitatively correct over an unreasonably wide range.
- Rigidity can be attributed to constraints implied by nodal structure of wavefunction – encapsulated by **Landau's Fermi liquid theory**.
- However, electron interactions can induce striking modifications in ground state reflected in novel experimental behaviour

  Electron localization – Mott transition; local moment and itinerant magnetism; quantum Hall fluids; and superconductivity.
- Such phases, which by their nature, lie outside any perturbative scheme built around the non-interacting ground state, underpin the field of modern quantum condensed matter and solid state physics.

Molecular spectra

Having established a basic formalism to describe molecular structure, we turn now to consider excitations and (radiative) transitions.

- These can include transitions between electron states (typically $\mathcal{O}(eV)$ – optical) as well as rotational/vibrational excitations.
- Usually electronic transition induces motion of nuclei as well.
- Energies of rotational states, $\mathcal{O}(\hbar^2/2I)$, are much smaller than those of electron excitations.
- Typical rotational energies are $\mathcal{O}(10^{-4}\mathrm{eV})$ (far IR) and vibrational excitations are $\mathcal{O}(10^{-1}\mathrm{eV})$ (cf. "Greenhouse effect").
- All three types of transitions can occur radiatively, i.e. through emission or absorption of a photon of frequency $\nu = \Delta E/h$.

Molecular spectra: transitions

- As with atoms, most probable radiative transitions are electric dipole, i.e. usual selection rule applies:

  $$\boxed{\Delta J = 0, \pm 1, \qquad \text{but not } 0 \rightarrow 0}$$

  accompanied by change in the parity of the molecular state.

- In a gas or liquid, transitions can also be produced by collisions. Such non-radiative transitions do not have to obey selection rules, i.e. molecule in a "metastable state" can be de-excited by collision.

- Collisions lead to thermal distribution of molecular energy levels,

  $$\boxed{n_i \propto g_i \exp\left[-\frac{E_i}{k_\mathrm{B} T}\right]}$$

  where g_i is degeneracy and E_i the energy. At room temperature, $k_\mathrm{B} T \sim 2 \times 10^{-2}$ eV, many rotational states of molecules are excited, but not electronic or vibrational.

Born-Oppenheimer approximation revisited

How can rotational/vibrational excitation spectrum be computed?

- Armed with Born-Oppenheimer approximation for electron states, ψ_k, we can exploit completeness to express full stationary state as

$$\boxed{\Psi(\{\mathbf{r}_n\},\{\mathbf{R}_N\}) = \sum_k \phi_k(\{\mathbf{R}_N\})\psi_k(\{\mathbf{r}_n\},\{\mathbf{R}_N\})}$$

  where ϕ_k represents the nuclear part of the wavefunction.

- Substituting into full time-independent Schrödinger equation,

$$\sum_k \left[\sum_{N=a,b,\dots} \frac{\hat{\mathbf{p}}_N^2}{2m_N} + \sum_{n=1,2,\dots} \frac{\hat{\mathbf{p}}_n^2}{2m_e} + V(\{\mathbf{r}_n\},\{\mathbf{R}_N\})\right] \Psi(\{\mathbf{r}_n\},\{\mathbf{R}_N\})\phi_k\psi_k$$

$$= E\Psi(\{\mathbf{r}\},\{\mathbf{R}_N\})\sum \phi$$

Born-Oppenheimer approximation revisited

$$\sum_k \left[\sum_{N=a,b,\ldots} \frac{\hat{\mathbf{p}}_N^2}{2m_N} + E_k(\{\mathbf{R}_N\}) \right] \phi_k \psi_k = E \sum_k \phi_k \psi_k$$

- Now, since dependence of $\psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$ on $\{\mathbf{R}_N\}$ is weak compared with that of the nuclear part $\phi_k(\{\mathbf{R}_N\})$, we can write

$$\nabla_N^2 \phi_k \psi_k \simeq \psi_k \nabla_N^2 \phi_k$$

- Using the orthogonality of ψ_k, we can pick out the $k = 0$ term,

$$\int \psi_0^* \sum_k \psi_k \left[- \sum_{N=a,b,\ldots} \frac{\hbar^2}{2m_N} \nabla_N^2 + E_0(\{\mathbf{R}_N\}) \right] \phi_k = E \int \psi_0^* \sum_k \psi_k \phi_k$$

$$\boxed{\left[- \sum_{N=a,b,\ldots} \frac{\hbar^2}{2m_N} \nabla_N^2 + E_0(\{\mathbf{R}_N\}) \right] \phi_0 = E \phi_0}$$

- i.e. ϕ_0 satisfies Schrödinger equation in which $V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$ is

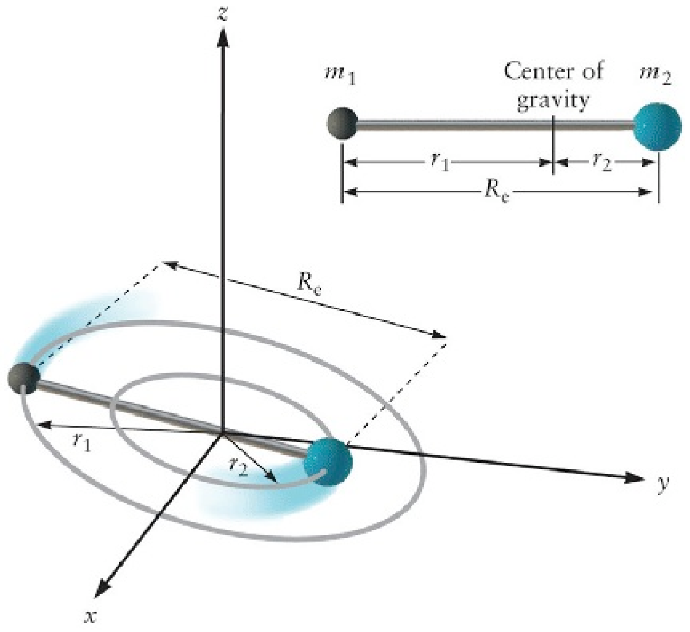
Molecular rotation

- Schrödinger equation for nuclear motion has many solutions, which give various molecular energy levels for given electron configuration.

- For diatomic molecules, $E_0(\mathbf{R}_1, \mathbf{R}_2) = E_0(R)$ where $R = |\mathbf{R}_1 - \mathbf{R}_2|$.
- Separating variables, Schrödinger equation of relative motion,

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{R}} + E_0(R)\right]\phi_0 = E\phi_0}$$

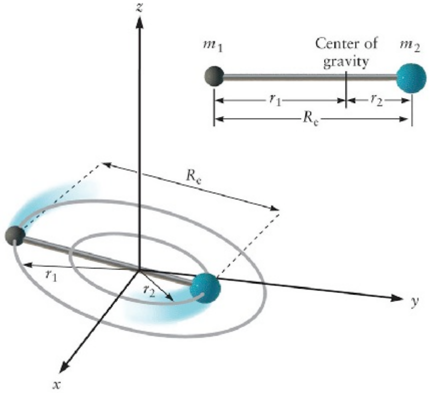
where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is reduced mass.



- $E_0(R)$ acts as a central potential, and the usual separation into angular and radial equations can be carried out.

Molecular rotation

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{R}} + E_0(R)\right]\phi_0 = E\phi_0}$$



- In lowest radial state, rotational energy levels described by usual spherical harmonic functions Y_{J,m_J}, with

  $$\boxed{E_J = \frac{\hbar^2}{2I}J(J+1)}$$

  where $I = \mu R_0^2$ is moment of inertia of molecule, and R_0 is equilibrium bond length.
- Since molecular dimensions set by Bohr radius a_0, $I \sim m_N a_0^2$ $E_J \sim \hbar^2/m_N a_0^2$.
- For the electron states, $p_e \sim \hbar/a_0$ and electron energies are ca. $\hbar^2/m_e a_0^2$, a factor of $m_N/m_e \sim 10^4$ greater.

Molecular rotation: transitions

- To bring about a radiative rotational transition, an emitted or absorbed photon must interact with the electric dipole moment of the molecule.
- Since the initial and final electronic states are the same, this state needs to have a permanent electric dipole moment.
- Therefore, can have rotational radiative transitions in **heteronuclear** diatomic molecules (e.g. HCl and CO), which have permanent dipole moments, but not in **homonuclear** (e.g. H_2 and O_2).
- Usual electric dipole selection rules apply: $\Delta J = \pm 1, 0$; but requirement for parity change excludes $\Delta J = 0$.

$$\boxed{\Delta E_{J \to J+1} = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] = \frac{\hbar^2}{I}(J+1)}$$

Molecular vibrations

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{R}} + E_0(R)\right]\phi_0 = E\phi_0}$$

- For a diatomic molecule, can Taylor expand molecular potential $E_0(R)$ around the equilibrium nuclear separation R_0,

$$E_0(R) = E_0(R_0) + \frac{1}{2}(R-R_0)^2\partial_R^2 E_0|_{R_0} + \ldots$$

- Leads to approximate harmonic oscillator with $\omega = (\frac{1}{\mu}\partial_R^2 E_0|_{R_0})^{1/2}$,

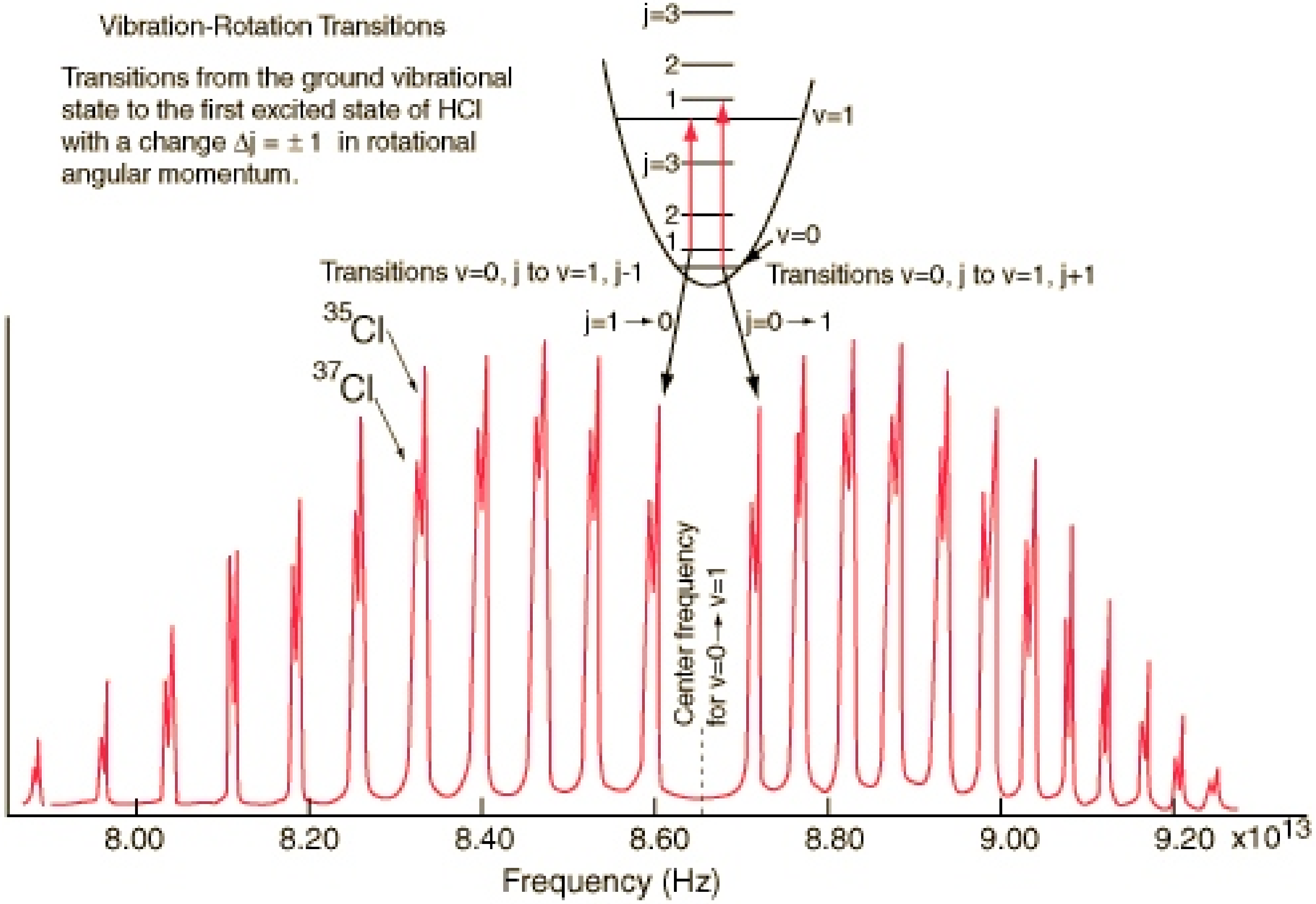
$$E = E_0(R_0) + (n+1/2)\hbar\omega, \qquad n = 0, 1, 2, \ldots$$

- Vibrational excitations typically larger than rotational by $\sqrt{m_N/m_e}$ and smaller than electronic excitations by $\sqrt{m_e/m_N}$ (see notes).
- Vibrational transitions: dipole selection rule (exercise), $\Delta n = \pm 1$, i.e. only a single energy in the spectrum,

$$\boxed{\Delta E = (E_{n+1} - E_n) = \hbar\omega}$$

Example: Rotation-vibration spectrum of HCl

$$\boxed{\Delta E = \hbar\omega + \frac{\hbar^2}{I}(J+1)}$$



Vibration-Rotation Transitions

Transitions from the ground vibrational state to the first excited state of HCl with a change $\Delta j = \pm 1$ in rotational angular momentum.