

Quantum Physics 2011/12

Tutorial Sheet 7: Bonding and Identical Particles

You may use the standard Gaussian integrals:

$$\int_0^\infty \exp(-\alpha^2 x^2) dx = \sqrt{\pi}/2\alpha$$

$$\int_0^\infty x \exp(-\alpha^2 x^2) dx = 1/2\alpha^2$$

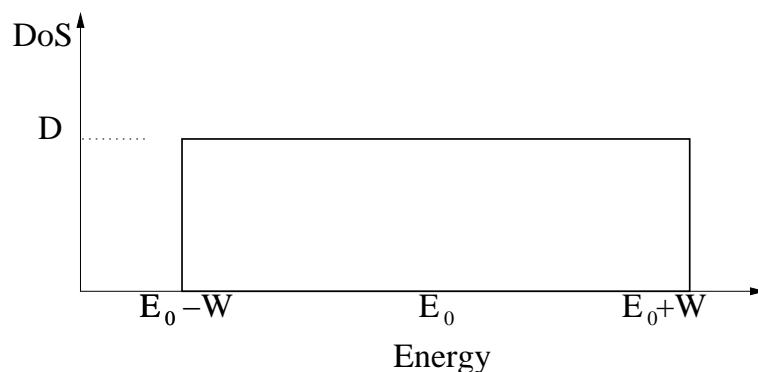
$$\int_0^\infty x^2 \exp(-\alpha^2 x^2) dx = \sqrt{\pi}/4\alpha^3$$

$$\int_0^\infty x^2 \exp[-(x-b)^2] dx = \frac{1}{4} [2be^{-b^2} + 2b^2\sqrt{\pi}\text{erf}(b) + \sqrt{\pi}\text{erf}(b) + 2b^2\sqrt{\pi} + \sqrt{\pi}]$$

$$\int x \exp[-(x-b)^2] dx = -\frac{1}{2} \exp(-x^2 + 2bx - b^2) - \frac{b}{2}\sqrt{\pi}\text{erf}(b-x)$$

1. The 4s conduction electron is bound to a Potassium ion with energy E_0 . A K_2^+ ion can be formed in exactly the same way as H_2^+ . With reference to your notes on H_2^+ , sketch the variation of energy with atomic separation for a K_2^+ molecule with a 4s conduction electron. On the same graph, without evaluating any integrals, sketch the energies for K_2^+ molecule with a 4p conduction electron (ignore degeneracy and assume only one p-level is involved in the bond). Explain why the electronic density of states for a gas of K_2^+ molecules formed from 4s atomic orbitals comprises delta functions, and sketch it taking the atomic energy as zero. What is the integral of the density of states per atom? How many of these states have lower energy than separated ion and atom?

When many ions are brought together in a solid, ignoring interactions between the ions and considering only 4s electrons, the density of states per atom becomes continuous and we can approximate it by a rectangle centred on the 4s atomic energy level.



Calculate the density of states, D , per atom in this figure. What are the units of D ?

Assuming that each K atom contributes one electron, calculate the cohesive energy of potassium due to filling of the density of states?

In the more general case of transition metals, the d-band DoS integrates to 10, and there are n_d electrons per atom. How does the cohesive energy (difference between free atom and atom in a solid) vary with n_d ?

2. A system comprises a particle moving in two 1D Simple Harmonic potentials separated by a distance $2R$, whose centres repel. Its Hamiltonian can be written

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(x) + 1/R$$

$$V(x) = \text{Min} \left(\frac{1}{2} m \omega^2 (x - R)^2, \frac{1}{2} m \omega^2 (x + R)^2 \right)$$

What is the expectation value of the energy for a single SHO ground state wavefunction at one site?

Assuming that the ground state wavefunction can be approximated by a linear combination of single SHO wavefunctions at each site, write down the appropriate wavefunction combinations for eigenstates with definite parity

Hence, evaluate the energy of the ground state.

Explore the limits $R \rightarrow 0$ and $R \rightarrow \infty$. Without further calculation, evaluate the energy of the first three excited states in the limit $R \rightarrow \infty$.

3. Four monovalent ions, with attractive potential $V(r)$ are arranged in a tetrahedron with edglength R . The ground state for electrons on the isolated ions is $u_0(r)$, positive everywhere. Write down the Hamiltonian matrix describing the electronic system in the LCAO approximation, ignoring electron-electron interactions and assuming that all three-centre integrals are zero.

Evaluate the four-electron wavefunctions in the LCAO approximation

By considering the sign of the integrals $V_{ij} = \langle u(\mathbf{r} - \mathbf{R}_i) | V(\mathbf{r} - \mathbf{R}_j) | u(\mathbf{r} - \mathbf{R}_j) \rangle$, where \mathbf{R}_i and \mathbf{R}_j are the positions of ions i and j , show that the ground state energy of the tetrahedron is

$$4E_0 + 12\Delta E + 4V_{12}$$

where

$$\begin{aligned} E_0 &= \langle u_0(r) | H_0(r) | u_0(r) \rangle \\ \Delta E &= \langle u_0(r) | V(r - R) | u_0(r) \rangle \\ V_{12} &= \langle u_0(r - R) | -\hbar^2 \nabla^2 / 2m + V(r) + V(r - R) | u_0(r) \rangle \end{aligned}$$

and that this has lower energy than the separated atoms or of two diatomic molecules.

Given the above, explain qualitatively why hydrogen forms diatomic molecules rather than tetrahedra?