Quantum Physics 2011/12

Solutions to Tutorial Sheet 7:

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?*

The spatial wavefunctions can be treated in the same way as H_2^+, leading to gerade and ungerade states.

$$E^{g,u}(\mathbf{R}) \;=\; \int \psi^{g,u*}(\mathbf{r},\,\mathbf{R})\,\hat{H}\,\psi^{g,u}(\mathbf{r},\,\mathbf{R})\,\mathrm{d}^3 r \;=\; \langle u_{4s}(r_1)|\hat{H}|u_{4s}(r_1)\rangle \pm \langle u_{4s}(r_1)|\hat{H}|u_{4s}(r_2)\rangle$$

$$E^{g,u}(\mathbf{R}) \;=\; \int \psi^{g,u*}(\mathbf{r},\,\mathbf{R})\,\hat{H}\,\psi^{g,u}(\mathbf{r},\,\mathbf{R})\,\mathrm{d}^3 r \;=\; \langle u_{4p}(r_1)|\hat{H}|u_{4p}(r_1)\rangle \pm \langle u_{4p}(r_1)|\hat{H}|u_{4p}(r_2)\rangle$$

Two 4p states can be combined similarly where u_{4p} is the atomic wavefunction. There is a shift of the energy for far-separated ions. Bonds between pairs of p-orbitals are referred to as π bonds, and are generally weaker than so-called σ-bonds between pairs of s-orbitals. Some molecules have both, while others have sp-bonding which combines s-orbitals with p-orbitals.
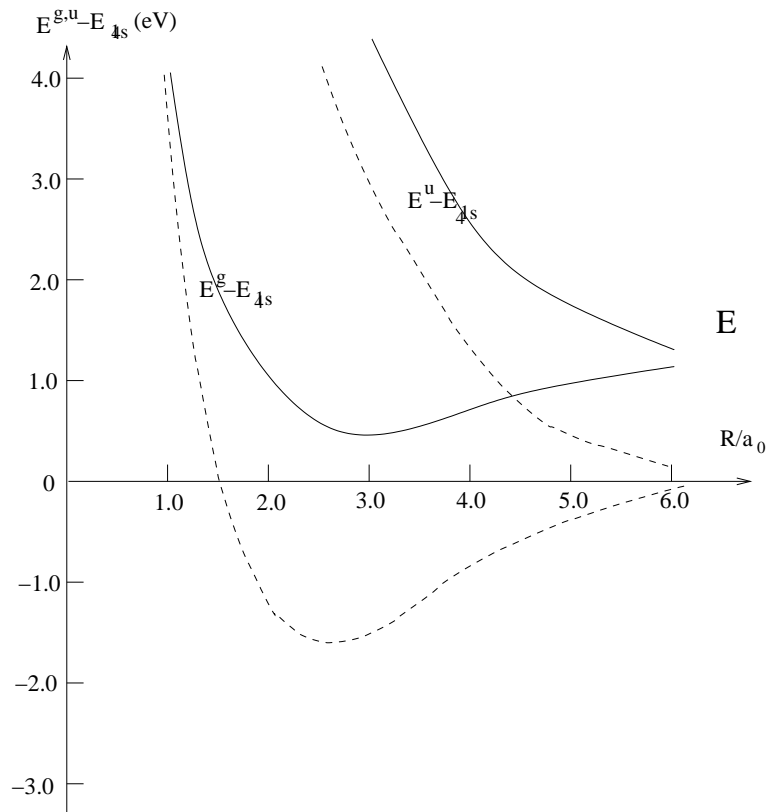
Thus there are only two possible distinct energies, so the density of states is simply two delta functions at E^g and E^u. Including spin, there are four possible states per molecular ion, so the integral of the density of states is 4 per ion, or two per atom. Only one state per atom (g) has lower energy than the separate components.

Note the skew in the energy shifts, the ungerade energy is further from the atomic energy than the gerade one. This is primarily due to including ion-ion repulsion in the energy. Note also that we are ignoring gerade bonding states made of linear combinations of $3d$-orbitals which have lower energy than the $4s$-ungrade case.
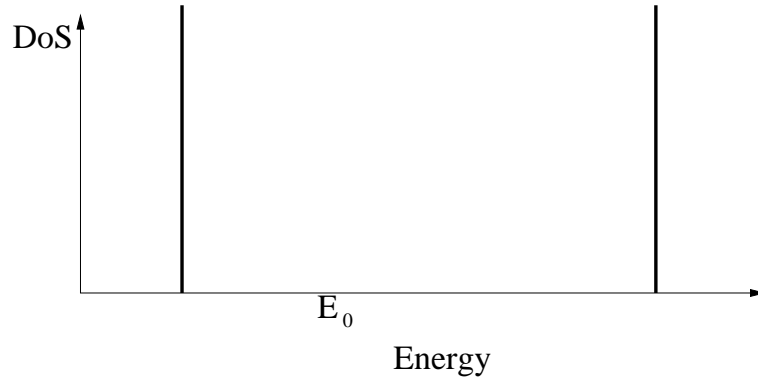
2. *When many ions are brought together, ignoring interactions between the ions, the density of states becomes continuous and we can approximate it by a rectangle.*
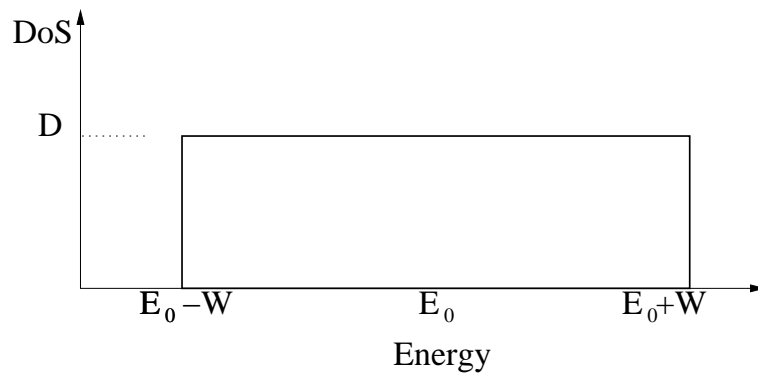
Calculate the density of states, D, per atom in this figure

The constant density of states is D. As before, since we are only considering $4s$ states, the integral of the density of states must be 2 electronic states per atom, hence $2WD = 2$ implies $D = 1/W$. This has units of "electronic states per atom per unit energy", e.g. eV^{-1}.

Assuming that each K ion contributes n electrons, calculate the cohesive energy of potassium due to filling of the density of states? By symmetry, the Fermi energy must be at E_0, so the cohesive energy (difference between atom and solid) is

$$\int_{E_0-W}^{E_0} D(E - E_0)dE = -W/2$$

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?

Now $2WD = 10$, so $D = 5/W$. First find the Fermi energy

$$\int_{E_0-W}^{E_F} D\,dE = n_d$$

$$E_F = E_0 + W\left(\frac{n_d}{5} - 1\right)$$

Now the cohesive energy is

$$\int_{E_0-W}^{E_F} D(E - E_0)\,dE = -W n_d\left(1 - \frac{n_d}{10}\right)$$

Thus the cohesive energy of transition metals varies parabolically across the band.

Ion-ion repulsion and Electron-electron repulsion have been ignored, what qualitative effect would they have?

Ion-ion repulsion is absent in the free atom, so will raise the energy of the solid, reducing cohesion. There is electron-electron interaction in both solid and atom near the ions, but the long range nature suggests that this effect will also reduce cohesion.

List other terms which have been ignored in this analysis

- Correlation energy
- Hybridization with other non d-states (incomplete basis in LCAO approximation)
- Non-degeneracy of the atomic d-levels
- Magnetic effects

3. *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*

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

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

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

The normalised ground state SHO wavefunction centred on R is:

$$u_0(x - R) = \sqrt{\frac{\alpha}{\sqrt{\pi}}}\exp-\frac{\alpha^2(x - R)^2}{2}$$

Defining $\hat{H}_0(x + R)$ as the SHO Hamiltonian centred at $x = -R$, we can write:

$$\hat{H} = \hat{H}_0(x + R) \qquad\qquad x < 0$$

$$\hat{H} = \hat{H}_0(x + R) - 2m\omega^2 xR \qquad x > 0$$

So that, since $\langle u_0(x + R)|\hat{H}(x + R)|u_0(x + R)\rangle = \frac{1}{2}\hbar\omega$:

$$\langle\hat{H}\rangle = \frac{1}{2}\hbar\omega - 2m\omega^2 R \frac{\alpha}{\sqrt{\pi}} \int_0^\infty x \exp -\alpha^2(x + R)^2 dx + \frac{1}{R}$$

The 1/R is just a constant which does not affect the wavefunction. Using the given integral

$$\langle H\rangle = \frac{1}{2}\hbar\omega + \frac{m\omega^2 R}{\sqrt{\pi}\alpha}\left(-\exp(-a^2 R^2) + \alpha R\sqrt{\pi}(1 - \mathrm{erf}(\alpha R))\right) + \frac{1}{R}$$

Note that for large R the second term goes to zero because the wells are far apart, while for small R it goes to zero because we revert to a single well.

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

The Hamiltonian is invariant under the parity operator $x \to -x$, thus the eigenfunctions must be a linear combination of the basis states:

$$\Phi_\pm(x) = (u_0(x + R) \pm u_0(x - R))/\sqrt{2}$$

Hence, evaluate the energy of the ground state.

The lowest energy state is the one without nodes, the symmetric (bonding) linear combination state:

$$\Phi_+ = \sqrt{\frac{\alpha}{2\sqrt{\pi}}}[\exp(-\frac{\alpha^2(x + R)^2}{2}) + \exp(-\frac{\alpha^2(x - R)^2}{2})]$$

for which the energy is the sum of direct and exchange terms: $H_{11} + H_{12}$. The anti-symmetric state has higher energy $H_{11} - H_{12}$.

The integrals we will need are:

$$H_{11} = \langle u_0(x + R)|\hat{H}|u_0(x + R)\rangle$$

$$H_{12} = \langle u_0(x - R)|\hat{H}|u_0(x + R)\rangle$$

The diagonal term H_{11} are exactly the same as for $\langle H\rangle$ in the first part of the question. The off diagonal term requires both kinetic and potential energy integrals.

$$H_{12} = T_{12} + V_{12}$$

$$T_{12} = \frac{-\hbar^2}{2m}\frac{\alpha}{\sqrt{\pi}}\int \exp -\frac{\alpha^2}{2}(x - R)^2 \frac{d^2}{dx^2}\exp -\frac{\alpha^2}{2}(x + R)^2 dx$$

$$= \frac{-\hbar^2}{2m} \frac{\alpha}{\sqrt{\pi}} \exp{-\alpha^2 R^2} \int \exp{-\alpha^2 x^2} [\alpha^4 x^2 - 2\alpha^4 x R + \alpha^4 R^2 - \alpha^2] dx$$

Using standard Gaussian integrals, and the fact that $\alpha^2 = m\omega/\hbar$

$$T_{12} = \hbar\omega(\frac{1}{4} - 2\alpha^2 R^2) \exp(-\alpha^2 R^2)$$

As a sanity check, note that as $R \to 0$ we recover the SHO result, while if the two potential wells are separated $R \to \infty$ the mixing term becomes zero.

Turning now to the potential energy

$$
\begin{aligned}
V_{12} &= \frac{1}{2} m\omega^2 \frac{\alpha}{\sqrt{\pi}} 2 \int_0^\infty (x-R)^2 \exp{-\frac{\alpha^2}{2}(x-R)^2} \exp{-\frac{\alpha^2}{2}(x+R)^2} dx & (1) \\
&= \frac{m\omega^2 \alpha}{\sqrt{\pi}} \exp(-\alpha^2 R^2) \int_0^\infty (x-R)^2 \exp(-\alpha^2 x^2) dx & (2) \\
&= \frac{m\omega^2 \alpha}{\sqrt{\pi}} \exp(-\alpha^2 R^2 ([\frac{\sqrt{\pi}}{4\alpha^3} - 2R\frac{1}{2\alpha^2} + \frac{\sqrt{\pi}}{\alpha} R^2] & (3) \\
&= \hbar\omega \exp{-\alpha^2 R^2}(\frac{1}{4} - \alpha R/\sqrt{\pi} + \alpha^2 R^2) & (4)
\end{aligned}
$$

So that:

$$H_{12} = \hbar\omega \exp(-\alpha^2 R^2) \left(\frac{1}{2} - \alpha R/\sqrt{\pi} - \alpha^2 R^2 \right)$$

and, including the repulsion between centres, the ground state energy becomes

$$
\begin{aligned}
E_0 &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega\alpha R}{\sqrt{\pi}\alpha} \left(-\exp(-a^2 R^2) + \alpha R\sqrt{\pi}(1 - \mathrm{erf}(\alpha R)) \right) \\
&\quad + \hbar\omega \exp(-\alpha^2 R^2) \left(\frac{1}{2} - \alpha R/\sqrt{\pi} - \alpha^2 R^2 \right) + 1/R
\end{aligned}
$$

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

As $R \to 0$ the potential becomes a single well SHO. The energy of the SHO ground state increases to $\hbar\omega$, but the $1/R$ term diverges, keeping the particles apart.

As $R \to \infty$, the ground state becomes that of the SHO, $\frac{1}{2}\hbar\omega$, as does the first excited state (two states, one in each oscillator). The second and third excited states must correspond to the $n = 1$ level of one of the SHOs, hence have energy $\frac{3}{2}\hbar\omega$

4. *Four monovalent ions, with attractive potential $V(r)$ are arranged in a tetrahedron with edgelength R. The ground state for electons on the isolated ions is $u_0(r)$, positive everywhere. Write down the Hamiltonian matrix describing the system in the LCAO approximation, assuming that all three-centre integrals are zero*

The Hamiltonian for this system is:

$$\frac{-\hbar^2}{2m}\nabla^2 + \sum_{i=1}^{4} V(\mathbf{r} - \mathbf{X_i})$$

We also define the isolated ion Hamiltonian:

$$H_0 = \frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

note that the ∇^2 operator is independent of the ion positions

The basis functions are $u_0(\mathbf{r} - \mathbf{X_i})$ for atom positions X_i $i = 1, 4$, corresponding to the single ion's Hamiltonian H_0.

We are assuming triple integrals like $\langle u_0(\mathbf{r} - \mathbf{X_i})|H_0(\mathbf{r} - \mathbf{X_j})|u_0(\mathbf{r} - \mathbf{X_k})\rangle$ are zero if i, j, k are all different.

Define

$$\langle u_0(r)|H_0(r)|u_0(r)\rangle = E_0$$

$$\langle u_0(r)|V(r - R)|u_0(r)\rangle = \Delta E$$

$$\langle u_0(r - R)| - \hbar^2 \nabla^2/2m + V(r) + V(r - R)|u_0(r)\rangle = V_{12}$$

and the one-electron Hamiltonian matrix becomes.

$$\begin{pmatrix} E_0 + 3\Delta E & V_{12} & V_{12} & V_{12} \\ V_{12} & E_0 + 3\Delta E & V_{12} & V_{12} \\ V_{12} & V_{12} & E_0 + 3\Delta E & V_{12} \\ V_{12} & V_{12} & V_{12} & E_0 + 3\Delta E \end{pmatrix}$$

Evaluate the wavefunctions in the LCAO approximation

This has eigenvectors, eigenvalues:

$$\frac{1}{2}(1, 1, 1, 1); \quad E_0 + 3\Delta E + 3V_{12}$$

$$\sqrt{\frac{1}{2}}(1, -1, 0, 0); \quad E_0 + 3\Delta E - V_{12}$$

$$\sqrt{\frac{1}{2}}(0, 0, 1, -1); \quad E_0 + 3\Delta E - V_{12}$$

$$\frac{1}{2}(-1, -1, 1, 1); \quad E_0 + 3\Delta E - V_{12}$$

The three degenerate states are not eigenstates of the tetrahedral symmetry operators: if that was required we would make linear combinations of them, which would also be solutions to the question as posed.

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

has lower energy than the separated atoms or of two diatomic molecules if electron-electron interaction is ignored

The first order perturbation term is

$$\Delta E = \int u_{100}(\mathbf{r})V(\mathbf{r} - \mathbf{R})u_{100}(\mathbf{r})d\mathbf{r}$$

and, the "hopping" term is

$$V_{12} = 2\int u_{100}(\mathbf{r} - \mathbf{R})V(\mathbf{r} - \mathbf{R})u_{100}(\mathbf{r})d\mathbf{r}$$

where the factor of 2 occurs because there are two terms which give identical (symmetry-equivalent) integrals.

u_{100} is positive everywhere, We are told that $V(\mathbf{r} - \mathbf{R})$ is attractive - i.e. negative. Thus ΔE and V_{12} come from integrating a negative quantity over space, so must both be negative. This tells us that the ground state is the symmetric $(1, 1, 1, 1)$ state with energy $E_0 + \Delta E + 3V_{12} < E_0$.

For monovalent ions we have four electrons, two in the $(1, 1, 1, 1)$ state (spin state $\uparrow\downarrow - \downarrow\uparrow$) and two in some linear combination of the degenerate states. The energy of this would be:

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

Which, given that ΔE and V_{12} are negative, has lower energy than the free atoms $4E_0$.

The molecules would have a one-electron Hamiltonian

$$\begin{pmatrix} E_0 + \Delta E & V_{12} & 0 & 0 \\ V_{12} & E_0 + \Delta E & 0 & 0 \\ 0 & 0 & E_0 + \Delta E & V_{12} \\ 0 & 0 & V_{12} & E_0 + \Delta E \end{pmatrix}$$

With doubly degenerate eigenvalues $E_0 + \Delta E \pm V_{12}$. Each state can hold two electrons of opposite spin, so all four electrons are in the lowest energy state (two covalent bonds) giving an energy. $4E_0 + 4\Delta E + 4V_{12}$, but this is still higher (not as strongly bound) as the tetrahedron.

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

Assuming three-centre orbitals are zero, and using the LCAO are both good approximations. But ignoring electron-electron and ion-ion repulsion is not, since they are comparable to the ion-electron interaction. The electron-electron and atom-atom repulsion is higher in the tetrahedron, and so whether the system forms molecules (like hydrogen) or solids (like lithium) depends on $V(r)$.