

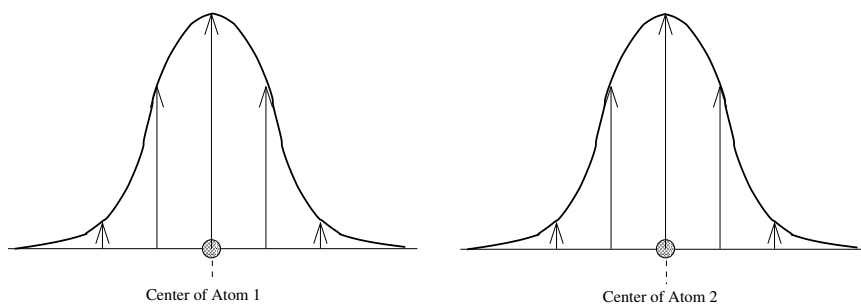
## Physics 008—Tutorial 7: Energy Bands

In this tutorial we are going to investigate how electronic bands form when atoms are brought together. We saw in the last tutorial and in the lectures that atoms possess discrete energy levels, which the electrons fill from the lowest level upwards.

When we examine what goes on when atoms are brought together, we find that we must look at the electronic wavefunctions themselves. As you remember, the wavefunctions describe the probability amplitude (length and direction of arrow) for an electron at all points in the 3D region of an atom. We will begin by simplifying the picture, by drawing the wavefunction in just one dimension.

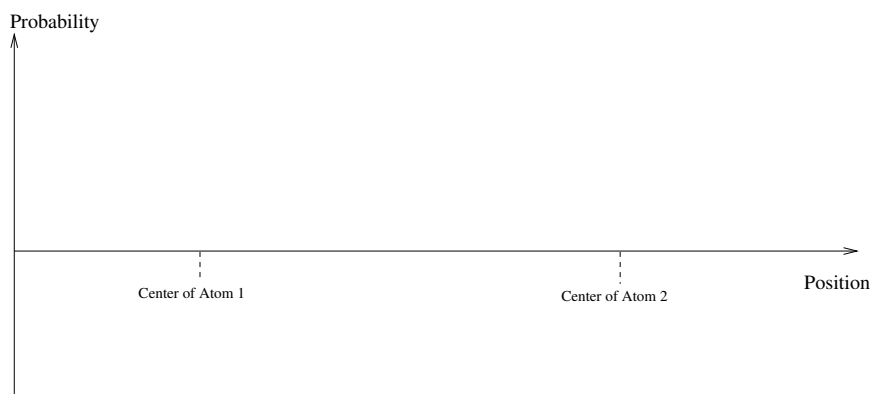
### 1 Two Atoms

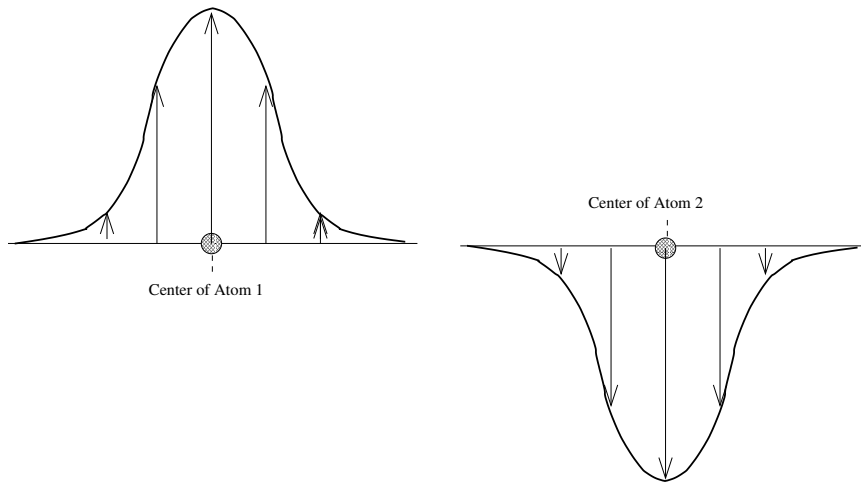
The figure below depicts the outermost electron wavefunctions of two separated atoms. As we saw in the particle in a box, there are two possibilities for the directions of the amplitude arrows - they can point in the same direction (say both at 12 o'clock) or in opposite directions (say one at 6 o'clock). Our first example has the arrows in the same direction.



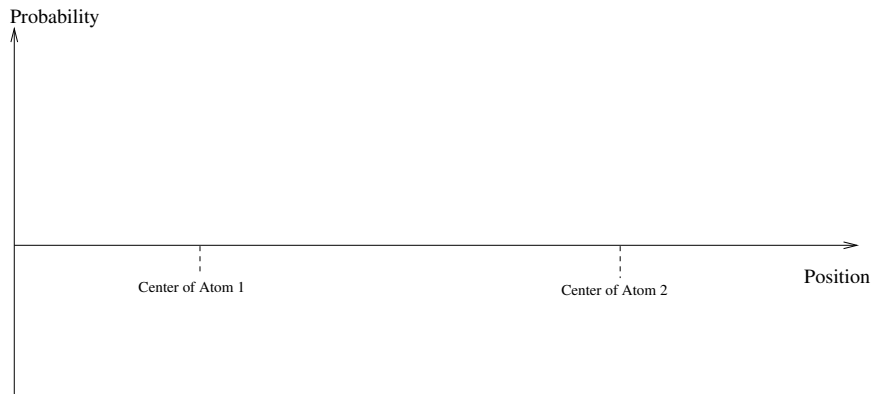
Notice that there is no overlap between the two wavefunctions, which shows that the presence of one has no effect on the other. If the energy of one atom is  $E_0$  in the ground state, what is the total energy of these two atoms in the ground state?

Sketch the probability distribution of the electrons in the two atoms.





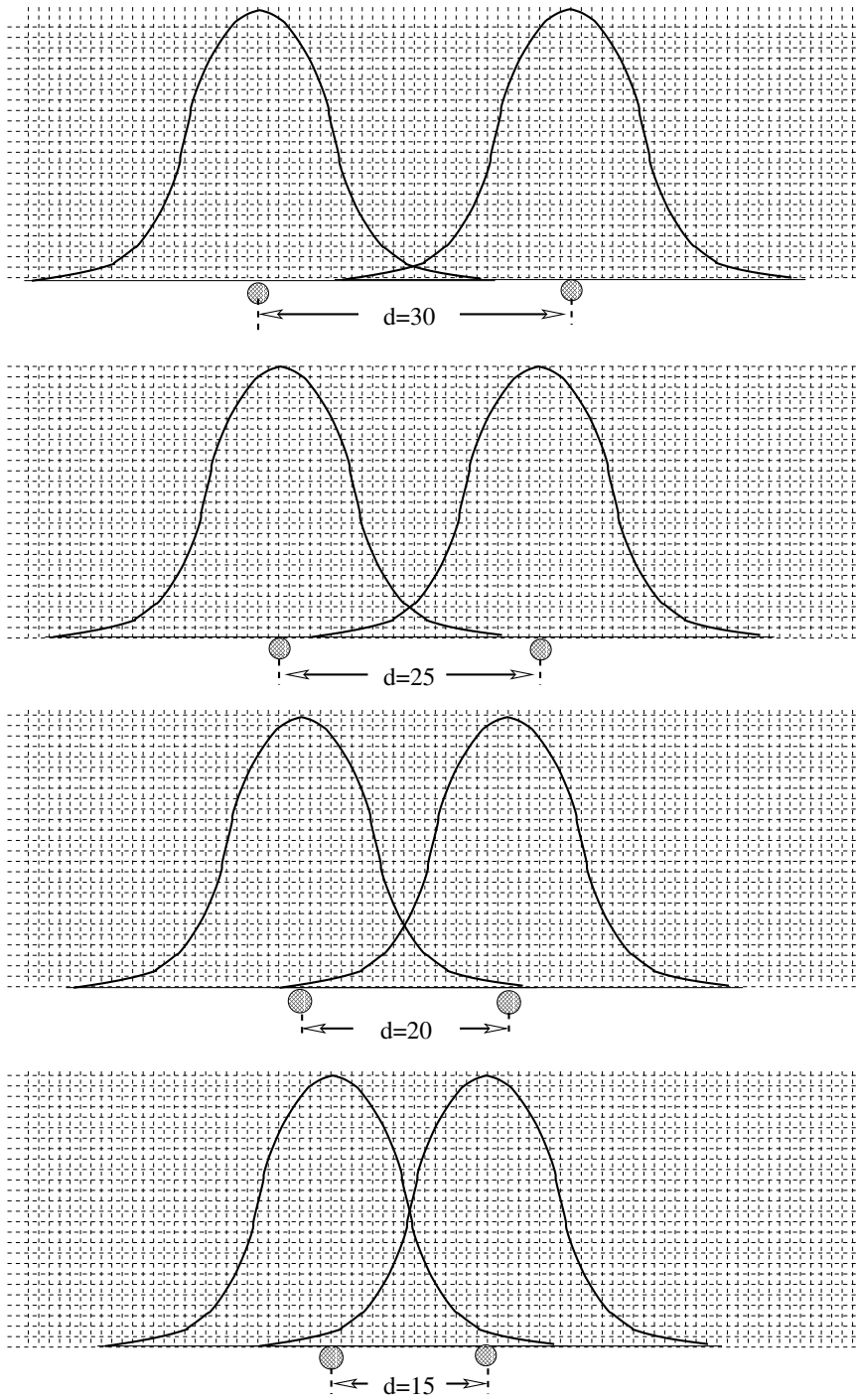
The second arrangement for the two wavefunctions is as shown. Sketch the probability distribution of the electrons in the two atoms. Is there any difference from the previous probability sketch?



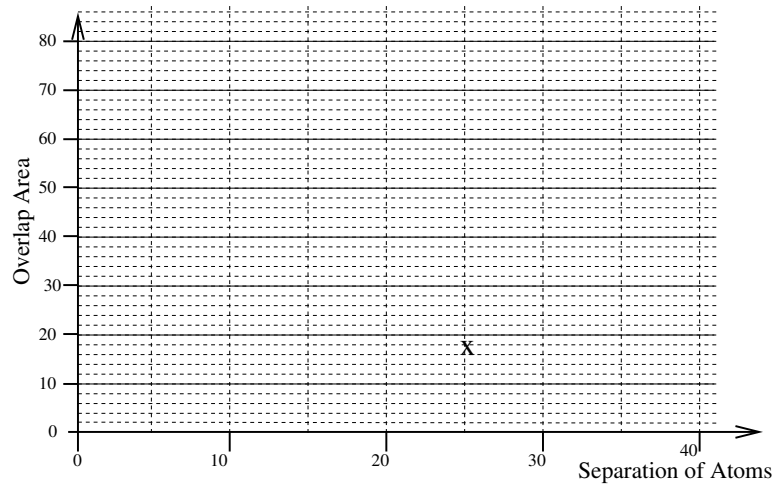
What is the energy for this case - how does it compare with your answer above? Explain.

As the atoms come closer together, there becomes a separation where the wavefunctions begin to overlap. The overlap can increase rapidly for a small change in the distance, as shown in the diagrams below.

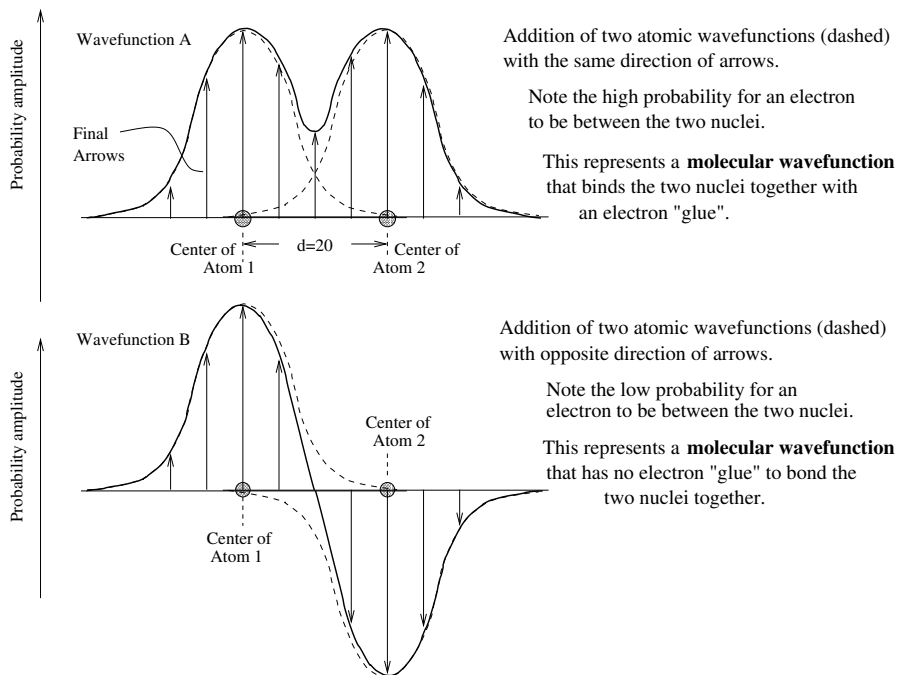
Estimate the overlap area for each separation shown by making a rough count of the number of squares under the two curves in the region where they have crossed.



Sketch the variation on the graph overleaf. As an example, the overlap area is approximately 17 for the separation  $d = 25$ . This point is already marked on the graph. Draw a smooth curve through your points.



Once the atoms are close enough for the wavefunctions to overlap, we can no longer think of there being different wavefunctions on separate atoms, because each electron can spend its time around both atoms. We look at the two possible combinations when the separation is equivalent to  $d=20$ . The final arrows are drawn in the diagram, each arrow corresponding to the sum of two amplitude arrows in the same direction (A) or opposite directions (B).



When there is a node in a wavefunction, the energy of an electron is affected just as if it could not cross that node. Bearing this in mind, compared to the wavefunction for a single atom, describe whether an electron in each of the above two wavefunctions is more spread out, or less spread out. (You might begin your discussion by considering the number of nodes in each.)

Is the kinetic energy of a single electron in wavefunction A more or less than its kinetic energy in a single atomic wavefunction?

How about the kinetic energy of a single electron in wavefunction B?

Two students are having a discussion about these wavefunctions.

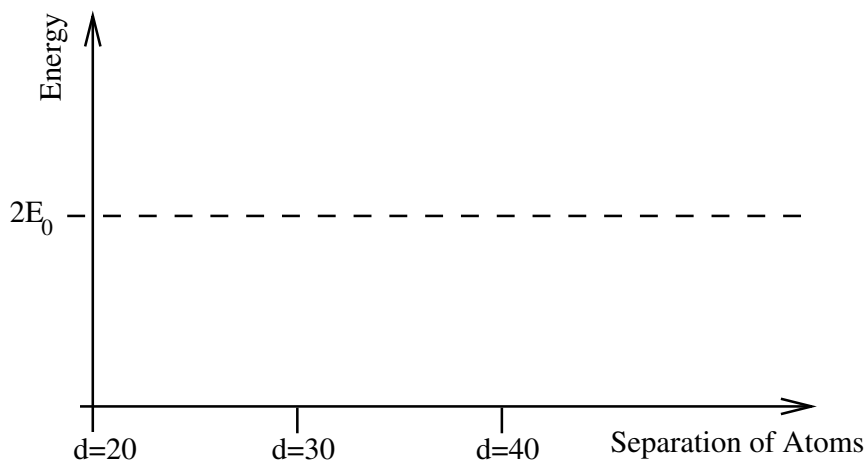
Daria: When the atoms are far away, the energy of the electrons is just equal to that of two separate atoms, but when they get closer, the energy of one molecular wavefunction increases and of the other decreases.

Quinn: I don't know, if the electrons are moving in a larger box, the uncertainty in their position is greater, so their kinetic energy should decrease. The energy for the molecule should be lower in both cases.

With which student do you agree? How does this observation explain why molecules form?

In general, as the overlap between atomic wavefunctions increases, so does the difference in energy between wavefunctions A and B.

On the graph below, sketch how the total energy of a molecule in which two electrons occupy wavefunction A depends on the separation of the two atoms. Do the same for the case where both electrons are in wavefunction B.

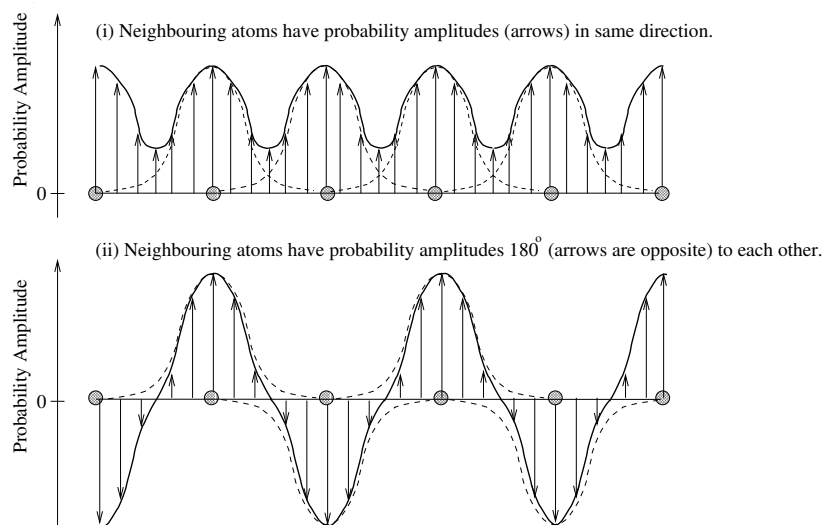


**Check answers with an instructor before proceeding further.**

## 2 Many Atoms in a Solid

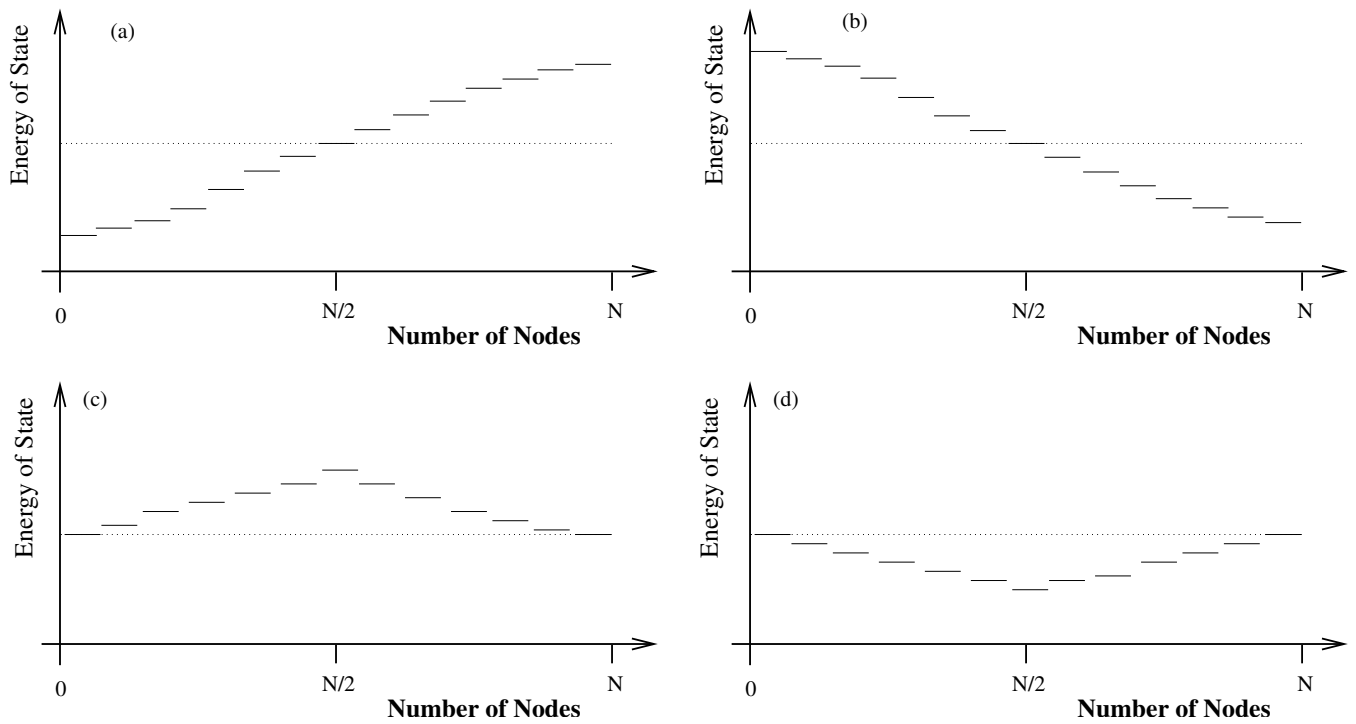
When a large number,  $N$ , of atoms come together, the wavefunctions can combine together with their probability amplitudes (arrows) rotated by any amount. For  $N$  atoms, there are  $N$  wavefunctions in total spread across all of the atoms (one for each atom). We will consider the two extreme cases, which show the **minimum number of nodes**, and the **maximum number of nodes**. This corresponds to neighbouring atoms with their stopwatch hands in the same direction, or rotated by an extra 6 hours to point up then down etc. as shown in the figure below. All the other combinations have the arrows rotating by some other angle, which would look like a 3D spiral if we let the arrows go into and out of the page. These spiral states have all energies between the maximum and minimum ones shown below, and we can think of them as having **any number of nodes**, from 1 to  $N-1$ .

In the diagram below, dashed lines represent the atomic wavefunctions, whose probability amplitudes (arrows) are added at each position to create each final arrow that is shown.



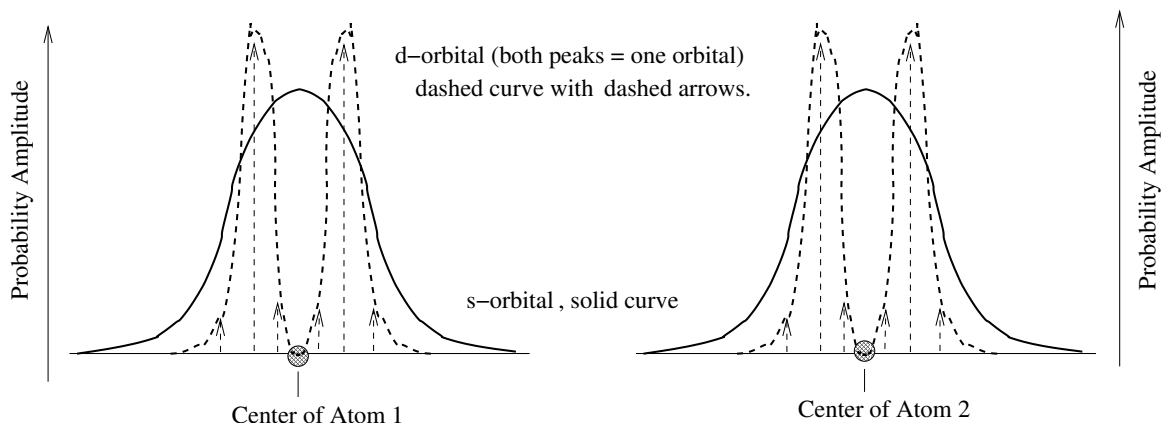
Which has lower energy, the state with **no nodes**, or the state with  **$N-1$  nodes**? Explain.

Below are four sketches of how the energy per atom could vary as the **number of nodes** is increased. The horizontal dotted line marks the energy of the wavefunction in an isolated atom. Which sketch is the correct one? Explain why the others are incorrect.



### 3 S-bands and d-bands in a Solid

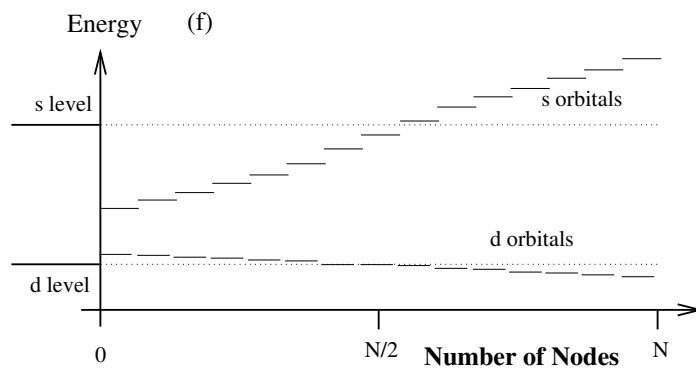
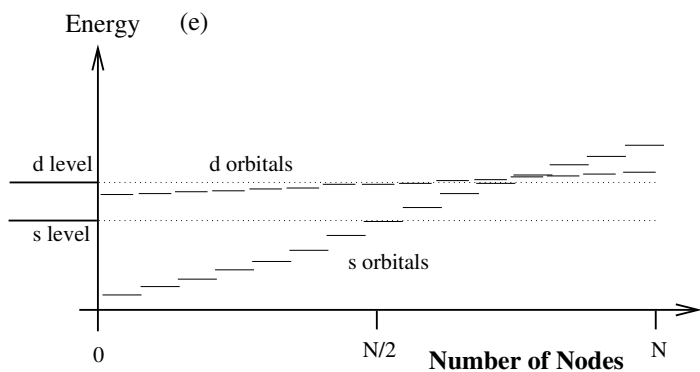
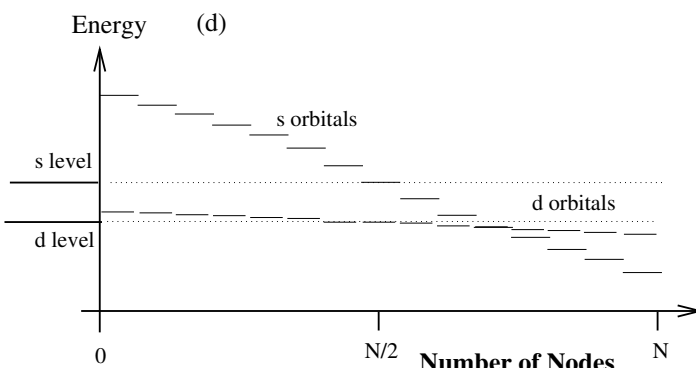
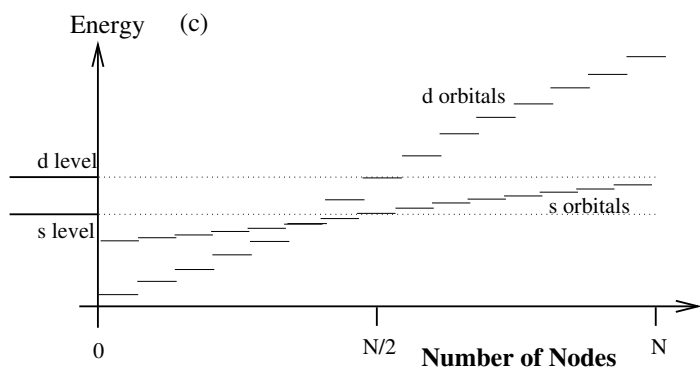
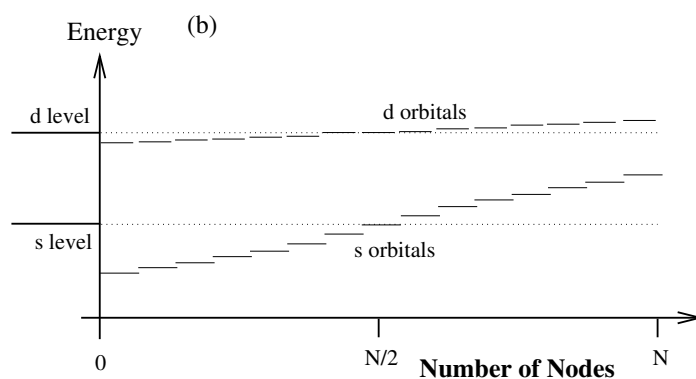
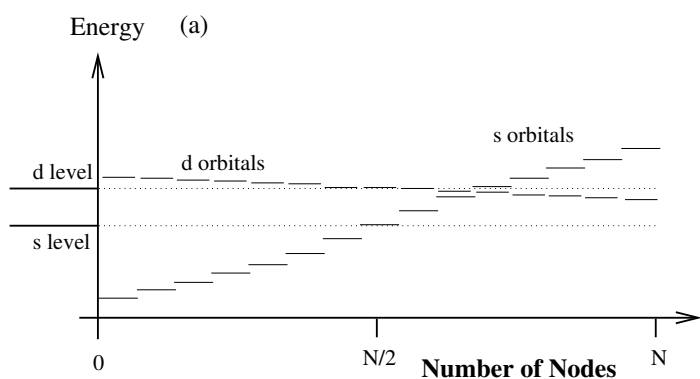
Figure 3 shows a sketch of an s-wavefunction and a d-wavefunction in each of two atoms.



When many of these atoms are brought together to form a solid, which wavefunctions (the s- or the d- ) will initially overlap more with those on neighboring atoms?

Which wavefunctions will have a larger spread in energies? (Hint: Review your plot on page 5. Assume the curves already plotted correspond to the energy of s-wavefunctions. Add curves for the d-wavefunctions.)

Using your results from the previous page, state which **two** diagrams below could represent the s-wavefunctions and d-wavefunctions in a solid, given the atomic s- and d- wavefunctions have the energies marked on the left of each diagram (and are dotted lines). Explain why the other **four** diagrams are incorrect.



**Check answers with an instructor before leaving!**