

CMP PS4

Richard Fern

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1

States in the Brillouin Zone

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal primitive lattice vectors have length a . Show that the number of different allowed k -states within the first Brillouin zone equals the number of primitive unit cells forming the specimen (do not consider spin). One may assume periodic boundary conditions, although it is worth thinking about whether this still holds for hard-wall boundary conditions as well.

This question is as easy as it sounds. These \mathbf{k} states are simply those of crystal momentum, and so they turn up in the form $e^{i\mathbf{k}\cdot\mathbf{x}}$. Therefore, given periodic boundary conditions we require

$$e^{ik_i(x_i+L)} = e^{ik_ix_i} \implies k_i = \frac{2\pi}{L}n.$$

Given that the first Brillouin zone extends a total distance of $\frac{2\pi}{a}$ then the number of states is

$$N_i = \frac{\frac{2\pi}{a}}{\frac{2\pi}{L}} = \frac{L}{a}.$$

This is in each direction so in total there are

$$N = N_x \times N_y \times N_z = \left(\frac{L}{a}\right)^3$$

states, the total number of unit cells.

For hard wall systems the eigenstates are more particle-in-a-box, so of the form $\prod_i \sin(k_i x_i)$. The width between k -states is the $\frac{\pi}{L}$ (because $\sin(k_i L) = 0$) and the Brillouin zone is $\frac{\pi}{a}$ in size ($x_i = na$ for some integer n_i so for $k_i \rightarrow k_i + \frac{\pi}{a}$ the state becomes $\sin(k_i x_i + \pi) = -\sin(k_i x_i)$ which is the same state).

2

Nearly Free Electron Model

Consider an electron in a weak periodic potential in one dimension $V(x) = V(x + a)$. Write the periodic potential as

$$V(x) = \sum_G e^{iGx} V_G$$

where the sum is over the reciprocal lattice $G = \frac{2\pi n}{a}$, and $V_G^* = V_{-G}$ assures that the potential $V(x)$ is real.

(a) Explain why for k near to a Brillouin zone boundary (such as k near $\frac{\pi}{a}$) the electron wavefunction should be taken to be

$$\psi = Ae^{ikx} + Be^{i(k+G)x} \quad (2.1)$$

where G is a reciprocal lattice vector such that $|k|$ is close to $|k + G|$.

For two states separated by some $\Delta E = E_1 - E_2$ which is roughly the same size as the perturbation, normal perturbation theory no longer works and we must use degenerate perturbation theory. For these purposes we take two nearly degenerate states which can be scattered into each other by the perturbation, as given here.

(b) For an electron of mass m with k exactly at a zone boundary, use the above form of the wavefunction to show that the eigenenergies at this wavevector are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \pm |V_G|$$

where G is chosen $|k| = |k + G|$.

We generate the matrix,

$$V = \begin{pmatrix} \langle A|V|A \rangle & \langle A|V|B \rangle \\ \langle B|V|A \rangle & \langle B|V|B \rangle \end{pmatrix} = \begin{pmatrix} V_0 & V_{-G} \\ V_G & V_0 \end{pmatrix}.$$

The eigenvalues of this are

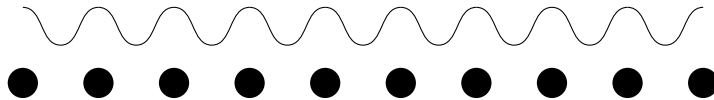
$$V_0 \pm |V_G|$$

and so the total energies (including the $\frac{\hbar^2 k^2}{2m}$) are indeed as given.

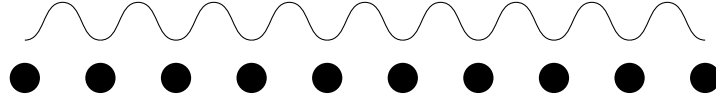
Give a qualitative explanation of why these two states are separated in energy by $2|V_G|$.

The electron wavefunctions form standing waves with wavelength $\frac{\pi}{a}$. The peaks of the lower energy wavefunction then sit at the positions where $V(x)$ is small and the peaks of the higher energy wavefunction are where $V(x)$ is large.

The low-energy wavefunction therefore looks like this.

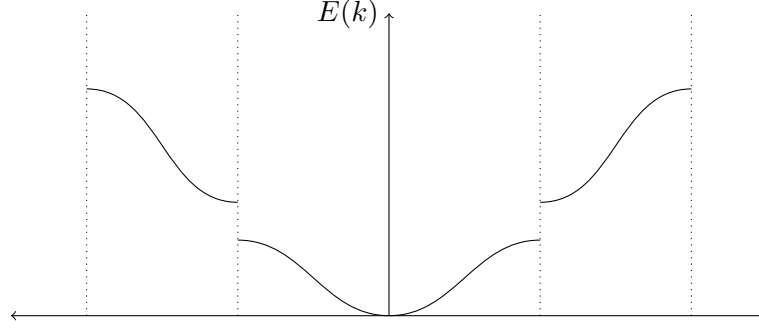


And the high energy one looks like this.

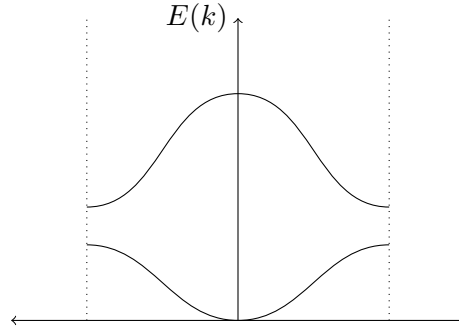


Give a sketch (don't do a full calculation) of the energy as a function of k in both the extended and reduced zone schemes.

In the extended zone scheme the dispersion is this.



In the reduced zone scheme it's this.



(In both cases the graph should only look significantly different from a parabola, or a folded parabola, near the BZ boundaries. This is not reflected so well here ...)

(c) Now consider k close to, but not exactly at, the zone boundary. Give an expression for the energy $E(k)$ correct to order δk^2 where δk is the wavevector difference of k to the zone boundary wavevector.

We do the same as before but must be careful to include the full Hamiltonian this time (as opposed to last time where we just used V). So

$$H = \begin{pmatrix} \langle A|H|A \rangle & \langle A|H|B \rangle \\ \langle B|H|A \rangle & \langle B|H|B \rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \delta k \right)^2 + V_0 & V_{-G} \\ V_G & \frac{\hbar^2}{2m} \left(-\frac{\pi}{a} + \delta k \right)^2 + V_0 \end{pmatrix}.$$

We diagonalise this using the equation

$$(T_+ + V_0 - E)(T_- + V_0 - E) = |V_G|^2$$

where T_{\pm} are the kinetic energies at $\pm \frac{\pi}{a}$. Thus,

$$E^2 - (T_+ + T_- + 2V_0)E = |V_G|^2 - (T_+ + V_0)(T_- + V_0).$$

Thus, using the quadratic formula and simplifying the square root term we reach

$$E = V_0 + \frac{T_+ + T_-}{2} \pm \sqrt{\left(\frac{T_+ - T_-}{2}\right)^2 + |V_G|^2}.$$

Now,

$$\frac{T_+ + T_-}{2} = \frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a}\right)^2 + \delta k^2 \right],$$

$$\frac{T_+ - T_-}{2} = \frac{\hbar^2}{m} \frac{\pi}{a} \delta k,$$

and therefore

$$\begin{aligned} E &= V_0 + \frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a}\right)^2 + \delta k^2 \right] \pm |V_G| \sqrt{1 + \left(\frac{\hbar^2 \pi}{ma|V_G|} \delta k\right)^2} \\ &= V_0 + \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 \pm |V_G| + \frac{\hbar^2}{2m} \left[1 \pm \frac{\hbar^2 \pi^2}{ma^2|V_G|} \right] \delta k^2. \end{aligned}$$

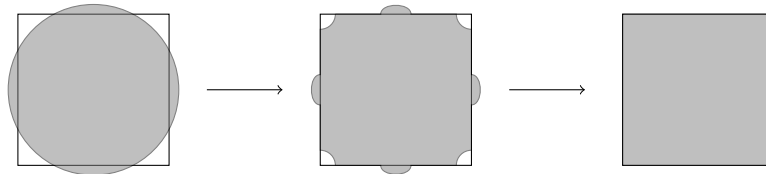
Calculate the effective mass of an electron at this wavevector.

The mass can be read off. It's just

$$m^* = \frac{m}{1 \pm \frac{\hbar^2 \pi^2}{ma^2|V_G|}}.$$

Consider a two dimensional square lattice with one divalent atom per unit cell. If the periodic potential is very very weak, you can consider the electrons to be free and to form a circular Fermi sea. Using the intuition from above (as well as the result of 4.1 above) sketch the Fermi surface for weak, medium and strong periodic potentials.

As the potential increases the Fermi surface looks like this.



Roughly how strong should the periodic potential be for a system to be no longer a metal?

The highest energy state is at $\frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a} \right)^2 + \left(\frac{\pi}{a} \right)^2 \right]$ and the lowest energy state (at the BZ boundary) is $\frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2$. Therefore, V_G must lower this corner state to make it lower than the side state, which gets raised by roughly V_G . So

$$2T - V_G < T + V_G \quad \implies \quad 2V_G > \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2.$$

Of course, these arguments are quite rough as they depend on V_G being small ... but it's an approximation.

What about the NFE model in 2D?

This is a little trickier. Clearly the points on the sides of the BZ are still only two-fold degenerate but the corners are fourfold degenerate (assuming we're on a square lattice). So take a cosine potential

$$V(x, y) = V \cos \left(\frac{2\pi}{a} x \right) + V \cos \left(\frac{2\pi}{a} y \right) = V (e^{iGx} + e^{-iGx} + e^{iGy} + e^{-iGy})$$

where I'm calling $G = \frac{2\pi}{a}$. So each corner is linked in this picture. The states are

$$\psi(\mathbf{r}) = \boldsymbol{\phi}^T \begin{pmatrix} e^{i\frac{G}{2}(x+y)} \\ e^{i\frac{G}{2}(x-y)} \\ e^{i\frac{G}{2}(-x+y)} \\ e^{i\frac{G}{2}(-x-y)} \end{pmatrix}$$

which sit at each corner. Thus, ignoring the kinetic energy term,

$$V = \begin{pmatrix} 0 & V & V & 0 \\ V & 0 & 0 & V \\ V & 0 & 0 & V \\ 0 & V & V & 0 \end{pmatrix}.$$

So, given the form of our potential, corners which share a side are scattered to each other by this potential. Let's find the eigenvalues. It's not bad in reality but I'll use a computer. We find

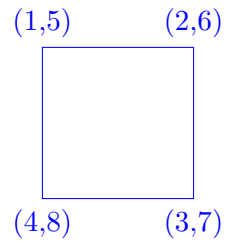
$$E = -2V, 0, 0, 2V.$$

3D?

Same thing. Let's take

$$V(\mathbf{r}) = V \cos \left(\frac{2\pi}{a} x \right) + V \cos \left(\frac{2\pi}{a} y \right) + V \cos \left(\frac{2\pi}{a} z \right).$$

So once again, they share only a side and so, using



where (i,j) refers to where we'll put the (upper,lower) wavefunctions sitting at those nodes in the BZ (remember we have a 3D cube). we find

$$\hat{V} = V \begin{pmatrix} 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 \end{pmatrix}.$$

Chuck this in a computer and we find

$$E = -3V, (-V, -V, -V), (V, V, V), 3V.$$

Cool.

3

Band Theory

- (a) Give a brief description of the formation of electron bands in crystals including reference to the atomic structure of the constituent atoms.

Think about small systems. For a molecule, we have a bond and an anti-bond as the orbitals of the two atoms are occupied in phase or in anti-phase, which gives us the ground state and an excited state. As we begin to add more and more atoms, we can have more and more possibilities with energies between the minimum and maximum, and these states are those of well-defined momentum which form bands. We can think of these states as described by electrons hopping between the orbitals in the lattice.

- (b) Explain the following:

- (i) sodium, which has 2 atoms in a BCC (conventional cubic) unit cell, is a metal;
- (ii) calcium, which has 4 atoms in a FCC (conventional cubic) unit cell, is a metal;
- (iii) diamond, which has 8 atoms in a FCC (conventional cubic) unit cell with a basis, is an electrical insulator, whereas silicon and germanium, which have similar structures, are semiconductors.

- (i) In the primitive unit cell there is one atom. Sodium is monovalent. Therefore, there are N electrons for $2N$ states per band, and so the band fills only halfway, leaving a Fermi surface which allows for conduction.
- (ii) Calcium has a primitive unit cell containing only one atom but is divalent. Therefore, there are $2N$ electrons which we might expect would fill the highest-energy band entirely. Therefore, in truth the bands must overlap somehow, much like in the nearly free electron model with a small $|V_G|$.
- (iii) Diamond has two atoms per primitive unit cell and has an even valence. Therefore, if the bands do not overlap (which they clearly don't) then there are enough electrons to totally fill the bands, leaving a gap and no Fermi surface. This does not allow for conduction. In Silicon and Germanium, the same must be true but the gap is clearly smaller.

Why is diamond transparent?

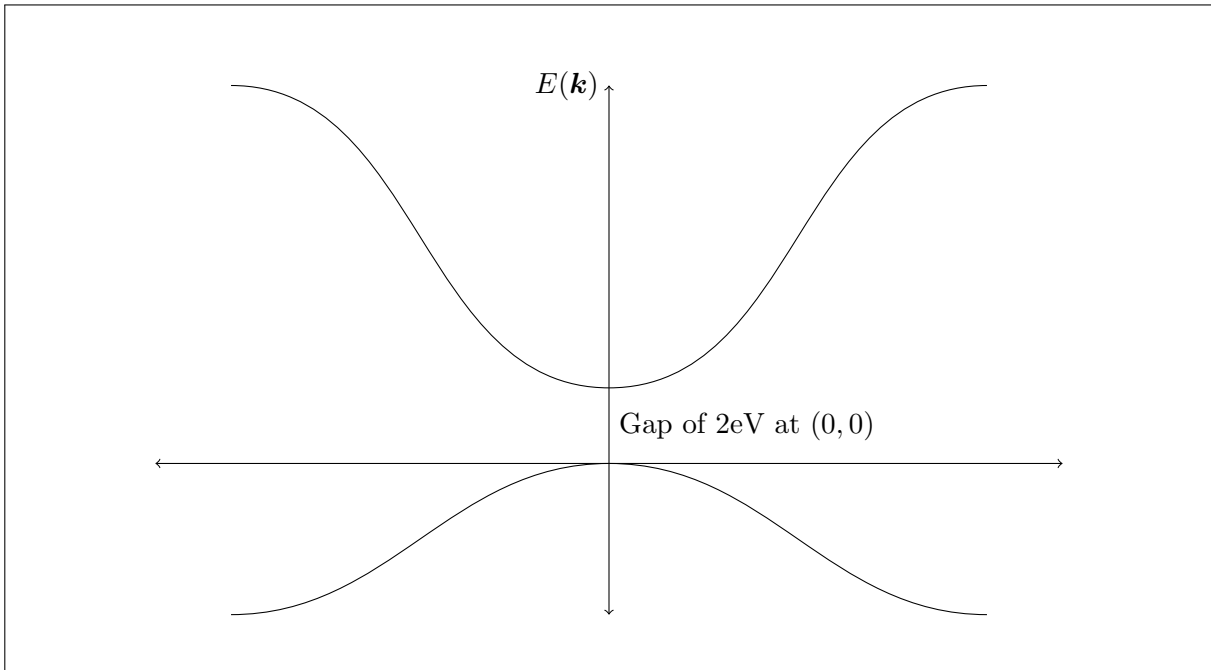
The gap in diamond must be larger than the energy of any photon of visible light. Therefore, a photon in the visible spectrum cannot excite any electrons in diamond as it passes through and must therefore pass through unimpeded (in a Fermi's golden rule argument, the density of final states for photons of visible light is zero so they cannot scatter).

- (c) A two-dimensional material has a square lattice with lattice constant $a = 0.3\text{nm}$. The dispersion relations for electron energies in the conduction and valence bands are given by

$$\epsilon_c(\mathbf{k}) = 6 - 2(\cos k_x a + \cos k_y a)$$

$$\epsilon_v(\mathbf{k}) = -2 + (\cos k_x a + \cos k_y a)$$

where energies are given here in units of eV. Sketch ϵ_c and ϵ_v for the direction $k_x = k_y$.



Indicate the value and position of the minimum band gap.

Done.

Show that close to the conduction and valence band edges, contours of constant energy are circles in k -space and determine the effective masses of both the electrons and holes.

In general

$$\epsilon = \epsilon_0 + t(\cos k_x a + \cos k_y a).$$

Now, it's not clear what edges means here so I'll assume it means edges in energy. Thus, expanding about $(0,0)$,

$$\epsilon = \epsilon_0 + t \left(2 - \frac{(k_x a)^2}{2} - \frac{(k_y a)^2}{2} + \dots \right) = \epsilon_0 + 2t - \frac{ta^2}{2} |\mathbf{k}|^2 + \dots$$

Thus, indeed the energy contours are circular, depending only on $|\mathbf{k}|$. Furthermore,

$$\frac{\hbar^2}{m^*} = |t|a^2 \quad \Rightarrow \quad m^* = \frac{\hbar^2}{|t|a^2}.$$

Therefore, for the valence and conduction bands

$$m^* = \frac{0.85\text{eV}}{|t|} m_e$$

$$\Rightarrow m_v^* = 0.85m_e, \quad m_c^* = 0.42m_e.$$

Sketch the density of states as a function of energy for the whole of both the conduction and the valence band.

The density of states is constant along k_x and k_y so

$$dN = \frac{A}{(2\pi)^2} d^2k.$$

To find the number of states at a given energy we must integrate this d^2k along lines of constant energy. Effectively, we need to know the length of a particular equipotential. Effectively we change from k_x, k_y to k_{\parallel}, k_{\perp} where k_{\perp} is perpendicular to ∇E and k_{\parallel} along it. Thus,

$$\frac{dN}{dE} = \frac{A}{(2\pi)^2} \frac{dk_{\parallel}}{dE} dk_{\perp}$$

where, by the definition of k_{\parallel} ,

$$\frac{dk_{\parallel}}{dE} = \frac{1}{|\nabla_{\mathbf{k}} E|}.$$

Thus, integrating finally around the equipotentials k_{\perp} ,

$$g(E) = \frac{A}{(2\pi)^2} \oint \frac{dk_{\perp}}{|\nabla_{\mathbf{k}} E|}.$$

(1) We can evaluate this at a few points and then guess the rest. Firstly, at the zone center, near $\mathbf{k} = 0$. Here,

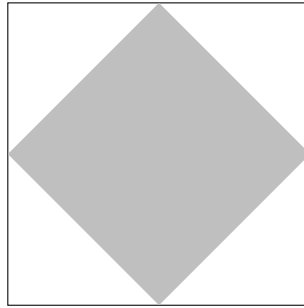
$$|\nabla_{\mathbf{k}} E| = |t|a^2|\mathbf{k}| \quad dk_{\perp} = |\mathbf{k}|d\theta.$$

Therefore,

$$g(E) = \frac{A}{2\pi|t|a^2},$$

which is constant. Therefore, the density of states starts of flat and then rises/falls. The same is true at the zone corners.

(2) We might also try to evaluate it at the middle of the band. If one thinks about it carefully one notices this is all those sites described by the following line.



So we can think about just one of the sides of this square (given the fourfold symmetry of the problem), where $k_x + k_y = \frac{\pi}{a}$. Thus,

$$|\nabla_{\mathbf{k}} E| = |t|a\sqrt{\sin^2 k_x a + \sin^2 k_y a} = |t|a\sqrt{2} |\sin k_x a|.$$

We wish to integrate the inverse of this along the side of this rectangle. We can simply do this by setting $dk_{\perp} = \sqrt{2}dk_x$ (this is one of those stare-at-it moments. We're trying

to integrate down the side of this square, which can easily be parameterised linearly by k_x . However, we need the $\sqrt{2}$ to account for the difference in length). So overall

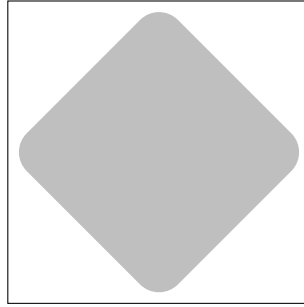
$$g(E) = \frac{A}{(2\pi)^2} 4 \times \int_0^{\frac{\pi}{a}} \frac{\sqrt{2} dk_x}{|t|a\sqrt{2} |\sin k_x a|}$$

$$= \frac{A}{\pi^2 |t| a^2} \int_0^{\pi} \frac{dx}{\sin x}.$$

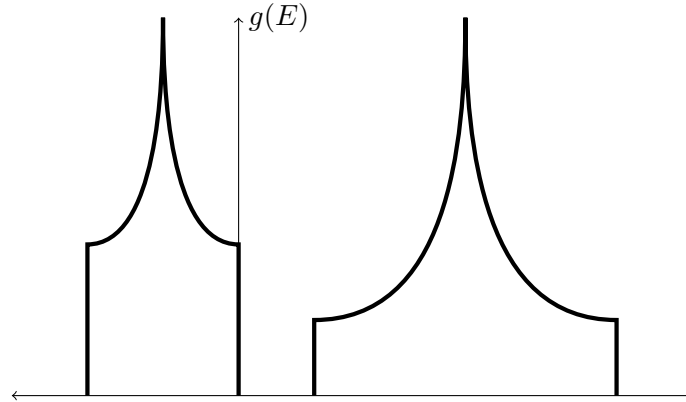
Plugging this into wolfram alpha we find

$$g(E) = \frac{A}{\pi^2 |t| a^2} \left[\ln \left(\cot x + \frac{1}{\sin x} \right) \right]_0^{\pi}.$$

This is therefore a logarithmically divergent point in the density of states as $\cot 0 = \cot \pi = \infty$. The points either side are unlikely to be similarly divergent as we might imagine they're described by almost the same integral except with the limits ever so slightly reduced as the equipotentials look more like this.



This is a conjecture though and the real problem is probably quite hard. Therefore, we can use this to draw our density of states. They're symmetric about the band middle, diverge at the middle and are constant at the sides.



Using a tight-binding Hamiltonian, explain where the above dispersion relations come from.

This is a tight binding Hamiltonian from two orbitals which appear not to talk. The higher energy orbital has a large amplitude to hop and this hopping lowers its energy. The lower energy orbital is less likely to hop and, strangely, hopping actually increases its energy. So

given orbital A and B

$$H = \sum_{\mathbf{n}, \mathbf{e}} \left[-2|A_{\mathbf{n}}\rangle\langle A_{\mathbf{n}}| + 6|B_{\mathbf{n}}\rangle\langle B_{\mathbf{n}}| + |A_{\mathbf{n}+\mathbf{e}}\rangle\langle A_{\mathbf{n}}| - 2|B_{\mathbf{n}+\mathbf{e}}\rangle\langle B_{\mathbf{n}}| \right]$$

where these $\mathbf{n} = (n_x, n_y)$ are the lattice vectors and $\mathbf{e} = (\pm 1, 0)$ or $(0, \pm 1)$ are the vectors to the nearest neighbours to which we hop to. t

4

Doping of Semiconductors

(a) Assume that the band gap energy E_g is much greater than the temperature $k_B T$. Derive expressions for the density of electron (n) and for the density of holes (p) and for the product np . Show that in a pure semiconductor at a fixed T , the product np depends only on the density of states in the conduction band and the density of states in the valence band (through their effective masses), and on the band gap energy. You may need to use the integral $\int_0^\infty dx x^{\frac{1}{2}} e^{-x} = \frac{\sqrt{\pi}}{2}$.

The number density of excited electrons in the conduction band is

$$n = \int dE g_c(E) \frac{1}{e^{\beta(E-\mu)} + 1}.$$

Assuming that $E - \mu \gg k_B T$ (as we expect $E - \mu$ to be of the order of E_g) we simplify this to

$$n = \int dE g_c(E) e^{-\beta(E-\mu)}.$$

We then treat the bottom of the band as a free electron system and so

$$\begin{aligned} \frac{dn}{dE} &= \frac{2}{(2\pi)^3} 4\pi k^2 \left(\frac{\hbar^2 k}{m_e} \right)^{-1} \\ &= \frac{1}{\pi^2} \frac{\sqrt{2} (m_e)^{\frac{3}{2}}}{\hbar^3} \sqrt{E - E_c} \end{aligned}$$

where E_c is the energy of the bottom of the band. Thus,

$$\begin{aligned} n &= e^{\beta\mu} \frac{1}{\pi^2} \frac{\sqrt{2} (m_e)^{\frac{3}{2}}}{\hbar^3} \int_{E_c}^\infty dE \sqrt{E - E_c} e^{-\beta E} \\ &= e^{-\beta(E_c-\mu)} \frac{1}{\sqrt{2}} \left(\frac{m_e}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}}. \end{aligned}$$

The same calculation holds for holes, except that $\mu > E_v$ so all the signs are reversed to give

$$p = e^{\beta(E_v-\mu)} \frac{1}{\sqrt{2}} \left(\frac{m_h}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}}.$$

Therefore,

$$np = \frac{1}{2} \left(\frac{\sqrt{m_h} \sqrt{m_e}}{\pi \hbar^2 \beta} \right)^3 e^{-\beta E_g},$$

which depends, as required, on only the densities of states and the band gap energy.

(b) The band gaps of silicon and germanium are 1.1eV and 0.75eV respectively. You may assume the effective masses for Silicon and Germanium are isotropic, roughly the same, and are roughly 0.5 of the bare electron mass for both electrons and holes (actually the effective masses are not quite the same, and furthermore the effective masses are both rather anisotropic, but we are just making rough estimates here).

Estimate the conduction electron concentration for intrinsic (undoped) silicon at room temperature.

When undoped we must have $n = p$. Therefore,

$$n = \frac{1}{\sqrt{2}} \left(\frac{\sqrt{m_h} \sqrt{m_e}}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} e^{-\beta \frac{E_g}{2}} = (8.66 \times 10^{24}) e^{-19.3 \times E_g}.$$

The numbers is therefore

$$n_{\text{Si}} = 5.3 \times 10^{15} \text{m}^{-3}.$$

Make a rough estimate of the maximum concentration of ionized impurities that will still allow for this “intrinsic” behaviour.

The number of ionised impurities must be much less than the number of electrons (or holes) to remain intrinsic.

Estimate the conduction electron concentration for germanium at room temperature.

$$n_{\text{Ge}} = 4.6 \times 10^{18} \text{m}^{-3}$$

(c) The graph in Figure 1 of the problem sheet shows the relationship between charge-carrier concentration for a certain n -doped semiconductor.

Estimate the bandgap for the semiconductor and the concentration of donor ions.

We make two readings. At $\frac{1}{T_1} = 0.0035$ $n_1 = 5 \times 10^{21}$. At $\frac{1}{T_2} = 0.005$ $n_2 = 4 \times 10^{20}$. These are made at high temperatures, so the semiconductor should be intrinsic. Therefore,

$$\frac{n_1}{n_2} = \left(\frac{T_1}{T_2} \right)^{\frac{3}{2}} e^{-\frac{\beta_1 - \beta_2}{2} E_g}$$

which we solve to find

$$E_g = \frac{2}{\beta_2 - \beta_1} \ln \left[\frac{n_1}{n_2} \left(\frac{\beta_1}{\beta_2} \right)^{\frac{3}{2}} \right] = 0.23 \text{eV}.$$

Describe in detail an experimental method by which this data could have been measured and suggest possible sources of experimental error.

A good way to measure low carrier concentrations in parabolic bands will be a Hall effect measurement. In this case the system is described very well by Drude theory. Therefore, the main sources of error include measuring voltages accurately, getting rid of contact resistance as much as is possible, aligning contacts, etc.

5

More Semiconductors

(a) In semiconductor physics what is meant by a “hole” and why is it useful?

A hole is the absence of an electron. It is far easier to think in terms of a positively charge absence with a filled background than it is to model the entire background in the presence of an absence. Furthermore, this absence (for very good reasons) acts almost exactly the same as an electron.

(b) An electron near the top of the valence band in a semiconductor has energy

$$E = -10^{-37}|\mathbf{k}|^2$$

where E is in J and k is in m^{-1} . An electron is removed from a state $\mathbf{k} = (2 \times 10^8)\text{m}^{-1}\hat{\mathbf{x}}$ where $\hat{\mathbf{x}}$ is the unit vector in the x -direction. For a hole, calculate (including the sign):

(i) the effective mass;

Effective masses are positive by definition. So

$$m = \frac{\hbar^2}{2 \times 10^{-37}} = 0.06m_e.$$

(ii) the energy;

It sits in the state with energy

$$E_{\text{state}} = -0.025\text{eV}$$

but the energy is positive because it took energy to remove the electron and therefore, the hole must have that energy.

$$E_h = 0.025\text{eV}.$$

(iii) the momentum;

The hole is the absence of an electron with this wavevector. Therefore, the momentum is the negative of that which the electron had,

$$\mathbf{p} = -\hbar\mathbf{k} = -2.1 \times 10^{-26}\text{kgms}^{-1}\hat{\mathbf{x}}.$$

(iv) the velocity.

The hole occupies the same state the electron did and therefore must evolve as the electron did. The state has group velocity $\mathbf{v} = \frac{1}{\hbar}\nabla_{|\mathbf{bm}\mathbf{k}}E$ and so the velocity is

$$\mathbf{v} = -380\text{kms}^{-1}\hat{\mathbf{x}}.$$

(v) If there is a density $p = 10^5 \text{m}^{-3}$ of such holes all having almost exactly this same momentum, calculate the current density and its sign.

Current is charge times velocity times concentration. The charges are positive, the velocities are negative, so

$$j = pev = -6.1 \times 10^{-9} \text{Am}^{-2}.$$

(c) Show that the chemical potential in an intrinsic semiconductor lies in the middle of the gap at low temperature.

Recall from the previous problem that we found

$$n = e^{-\beta(E_c - \mu)} \frac{1}{\sqrt{2}} \left(\frac{m_e}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}}.$$

However, we also found that for an intrinsic semiconductor

$$n = \frac{1}{\sqrt{2}} \left(\frac{\sqrt{m_h} \sqrt{m_e}}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} e^{-\beta \frac{E_g}{2}}.$$

We set these equal and solve for μ .

$$\begin{aligned} \beta\mu &= \ln \left[\left(\frac{m_h}{m_e} \right)^{\frac{3}{4}} e^{\beta(E_c - \frac{E_g}{2})} \right] \\ \mu &= E_c - \frac{E_g}{2} + \frac{3}{4\beta} \ln \frac{m_h}{m_e}. \end{aligned}$$

Therefore, as $\beta \rightarrow \infty$, this second term disappears and, indeed, the chemical potential sits at the halfway point in the gap.

Explain how the chemical potential varies with temperature if the semiconductor is doped with (i) donors (ii) acceptors.

As we add donors at low temperature the chemical potential is raised as extra states including electrons are added just below the conduction band. As the temperature is increased and the material becomes more intrinsic the formula we just derived becomes a better fit. Doping with acceptors does the opposite initially, reducing the chemical potential to the acceptor states just above the valence band, and then the same, converging to intrinsic behaviour.

(d) A direct gap semiconductor is doped to produce a density of $10^{23} \text{electron/m}^3$. Calculate the hole density at room temperature given that the gap is 1.0eV, and the effective mass of carriers in the conduction and valence band are 0.25 and 0.4 electron masses respectively.

We use our previous result

$$np = \frac{1}{2} \left(\frac{\sqrt{m_h} \sqrt{m_e}}{\pi \hbar^2 \beta} \right)^3 e^{-\beta E_g},$$

to find that $np = 3.34 \times 10^{32}$. Similarly, given the doping, $n = p + 10^{23}$ so

$$p^2 + 10^{23}p - 3.34 \times 10^{32} = 0.$$

Clearly we must take the $-$ solution of this (or the number of holes would be greater than electrons) and so we do an expansion (because my calculator isn't accurate enough) to find

$$\begin{aligned} p &= 0.5 \times 10^{23} - 0.5 \times 10^{23} \sqrt{1 - 1.33 \times 10^{-13}} \\ &= 3.3 \times 10^9 \text{ m}^{-3}. \end{aligned}$$

6

General Magnetism

(a) Explain qualitatively why some atoms are paramagnetic and other are diamagnetic with reference to the electronic structure of these materials.

Nobody likes a qualitative argument. So consider a Hamiltonian for an electron,

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + g\mu_B \mathbf{S} \cdot \mathbf{B}.$$

If we expand the $\mathbf{p} + e\mathbf{A}$ term, using the gauge choice $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ for a constant magnetic field then we will find

$$H = \frac{\mathbf{p}^2}{2m} + \frac{e}{2m} \mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) + g\mu_B \mathbf{S} \cdot \mathbf{B} + \frac{e^2}{8m} (\mathbf{B} \times \mathbf{r})^2.$$

In this middle term we can permute \mathbf{p} , \mathbf{B} and \mathbf{r} and use that the angular momentum is $\mathbf{r} \times \mathbf{p} = \hbar \mathbf{L}$. Therefore,

$$H = \frac{\mathbf{p}^2}{2m} + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m} (\mathbf{B} \times \mathbf{r})^2.$$

The second term in this equation is the paramagnetic term. We see that the electron wishes to anti-align its spin and angular momentum with the magnetic field, which aligns its magnetic moments along the field's direction ($\boldsymbol{\mu} = -\mu_B \mathbf{L}$).

The third term is the diamagnetic term. This is in general extremely small but dominates when the total moment of the atom is zero. It causes diamagnetism because the energy is increased by a field and so the electron will try to oppose this if possible, but can only do so very weakly.

(b) Define the terms Ferromagnetism, Antiferromagnetism, Ferrimagnetism and Itinerant Ferromagnetism.

- In ferromagnets the magnetic moments align to give a net magnetisation.
- An antiferromagnet anti-aligns neighbouring moments to give a net zero magnetisation but a magnetic order (which we can see in neutron scattering experiments)
- A ferrimagnet is much like an antiferromagnet in terms of its magnetic order but the anti-aligning moments are not equal in magnitude so there remains a net magnetisation.
- Itinerant ferromagnetism is the alignment of electrons which are free to move in the system.

Write down an example of a Hamiltonian which would have each of these as its ground state.

- For ferromagnets

$$H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

where $\langle i,j \rangle$ is a sum over nearest neighbours.

- For an antiferromagnet

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j.$$

- For a ferrimagnet,

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i^A \cdot \mathbf{S}_j^B$$

where $|\mathbf{S}^A| \neq |\mathbf{S}^B|$.

- For an itinerant ferromagnet we can consider the Hubbard model away from half filling. The Hubbard model is

$$H = U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

and just encodes on-site electron-electron repulsion. Add in a hopping term and consider away from half filling and the spins wish to order. Alternatively, RKKY interactions can mediate spin polarisation in a free electron sea.

Use Hund's rules and the Aufbau principle to determine L , S and J for the following isolated atoms:

(i) Sulfur (S), atomic number 16

This is reasonably easy. We just fill shells in order to give $1s^2 2s^2 2p^6 3s^2 3p^4$. Therefore, with 4 electrons in the p shell we align the three S and then pick the maximum L , with this S anti-aligned with the rest. The shell is then over half-full so $S = 1$, $L = 1$ and $J = 2$.

(ii) Vanadium (V), atomic number 23

Once again we fill up in turn but recall that $4s$ fills before $3d$ so the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. This can align all the spins so $S = \frac{3}{2}$. The maximum angular momentum we can get is then $L = 3$. The shell is under half-full so $J = \frac{3}{2}$.

(iii) Zirconium (Zr), atomic number 40

The configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$. Thus, $S = 1$, $L = 3$ and they anti-align so $J = 2$.

(iv) Xenon (Xe), atomic number 54

The configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$. The bands are filled so $S = L = J = 0$.

(v) Dysprosium (Dy), atomic number=66

After filling $6s^2$ the next orbital to fill is the f shell with 14 available states. So the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{10}$. Therefore, the hole spins align to give $S = 2$ and they maximise angular momentum so $L = 6$. This adds because we're over half-filling, so $J = 8$.

7 Para and Diamagnetism

Manganese (Mn, atomic number 25) forms an atomic vapour at 2000K with vapour pressure 10^5 Pa. You can consider this vapour to be an ideal gas.

(a) Determine L , S and J for an isolated manganese atom. Determine the paramagnetic contribution to the (Curie) susceptibility of this gas at 2000K.

The configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$. Thus $S = \frac{5}{2}$ but $L = 0$. Thus, $J = \frac{5}{2}$. We find the Curie susceptibility by applying a field and considering the partition function,

$$Z = \sum_{S=-\frac{5}{2}}^{\frac{5}{2}} e^{-\beta g \mu_B B S}.$$

We then recall that the free energy is $F = -k_B T \ln Z$ gives the magnetic moment as $M = -\frac{\partial F}{\partial B}$ (because $dF = -SdT - MdB$). Thus,

$$M = k_B T \frac{1}{Z} \sum_{S=-\frac{5}{2}}^{\frac{5}{2}} (-\beta g \mu_B S) e^{-\beta g \mu_B B S}.$$

We then wish to find the susceptibility of the form $M = \chi B$ so we expand everything to first order in B .

$$M = -g \mu_B \frac{\sum_{S=-\frac{5}{2}}^{\frac{5}{2}} S(1 - \beta g \mu_B B S)}{\sum_{S=-\frac{5}{2}}^{\frac{5}{2}} (1 - \beta g \mu_B B S)}.$$

As the sums over S are spin-flip symmetric, only even powers of S survive and so

$$M = \beta (g \mu_B)^2 B \frac{35}{12}.$$

Therefore,

$$\chi = \frac{35}{12 k_B T} (g \mu_B)^2.$$

A μ_0 is usually tacked onto this as we consider $\chi = \frac{\partial M}{\partial H}$ instead of B .

(b) In addition to the Curie susceptibility, the manganese atom will also have some diamagnetic susceptibility due to its filled core orbitals. Determine the Larmor diamagnetism of the gas at 2000K. You may assume the atomic radius of a manganese atom is one angstrom.

From earlier we saw that the energy change from the diamagnetic term was

$$\delta E = \frac{e^2}{8m} \langle (\mathbf{B} \times \mathbf{r})^2 \rangle.$$

Calculating the vector (setting \mathbf{B} along z) one find that this is

$$\delta E = \frac{e^2 B^2}{8m} \langle x^2 + y^2 \rangle,$$

which assuming the atom is isotropic is the same as

$$\delta E = \frac{e^2 B^2}{12m} \langle r^2 \rangle.$$

The moment created by this is therefore

$$M = \frac{d\delta E}{dB} = \frac{e^2}{6m} \langle r^2 \rangle B$$

and so the susceptibility (of a whole sample) is

$$\chi = \mu_0 \rho \frac{e^2}{6m} \langle r^2 \rangle$$

where ρ is the number density multiplied by the number of electrons, n , per manganese (23). We know that $n = \frac{p}{k_B T}$ and approximate $\langle r^2 \rangle \sim (10^{-10})^2$ so

$$\chi = 4.9 \times 10^{-9}.$$

8

Mean Field Theory of the Ferromagnet

Consider the spin- $\frac{1}{2}$ ferromagnetic Heisenberg Hamiltonian on the cubic lattice

$$\mathcal{H} = -\frac{J}{2} \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \mathbf{B} \cdot \sum_i \mathbf{S}_i.$$

Here, $J > 0$, the sum indicated by $\langle i, j \rangle$ means summing over i and j being neighbouring sites of the cubic lattice, and \mathbf{B} is the externally applied magnetic field (which we will assume is in the \hat{z} direction for simplicity). The factor of $\frac{1}{2}$ out front is included so that each pair of spins is counted only once. Each site i is assumed to have a spin \mathbf{S}_i of spin $S = \frac{1}{2}$. Here μ_B is the conventional Bohr magneton defined to be positive. The fact that the final term has a $+$ sign out front is from the fact that the electron charge is negative, therefore the magnetic moment opposes the spin direction. If one were to assume that these were nuclear spins the sign would be reversed (and the magnitude would be much smaller due to the larger nuclear mass).

(a) Focus your attention on one particular spin \mathbf{S}_i , and write down an effective Hamiltonian for this spin, treating all other variable \mathbf{S}_j with $j \neq i$ as expectation $\langle \mathbf{S}_j \rangle$ rather than operators.

$$H_i = \mathbf{S}_i \cdot \left(g\mu_B \mathbf{B} - J \sum_j \langle \mathbf{S}_j \rangle \right).$$

(b) Calculate $\langle \mathbf{S}_i \rangle$ in terms of the temperature and the fixed variables $\langle \mathbf{S}_j \rangle$ to obtain a mean-field self-consistency equation.

This is effectively just some spin in an effective field with energies $E = \pm \frac{1}{2} B_e$. So taking B along the z direction,

$$Z = 2 \cosh \left(\frac{1}{2} \beta B_e \right).$$

The expectation value of the spin along z is then simply $\langle S \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial (\beta B_e)}$

$$\langle S \rangle = -\frac{1}{2} \tanh \left(\frac{1}{2} \beta B_e \right).$$

Thus,

$$\langle S \rangle = -\frac{1}{2} \tanh \left(\frac{\beta}{2} (g\mu_B B - 6J \langle S \rangle) \right)$$

(where this 6 appears because there are 6 nearest neighbours on a cubic lattice).

Write the magnetisation $M = |\mathbf{M}|$ in terms of $\langle \mathbf{S} \rangle$ and the density of spins.

$$\mathbf{M} = -ng\mu_B \langle \mathbf{S} \rangle.$$

(c) At high temperature, find the susceptibility $\chi = \frac{dM}{dH} = \mu_0 \frac{dM}{dB}$ in this approximation.

This is the $\beta \rightarrow 0$ regime. We expand tanh and solve,

$$\begin{aligned}\langle S \rangle &= -\frac{\beta g \mu_B B}{4} + \frac{3\beta J \langle S \rangle}{2} \\ \langle S \rangle &= -\frac{g \mu_B}{4k_B T - 6J} B.\end{aligned}$$

Therefore,

$$\chi = \mu_0 n \frac{(g \mu_B)^2}{4k_B T - 6J}.$$

(d) Find the critical temperature in this approximation.

When the denominator is 0, any field polarises the entire sample. So

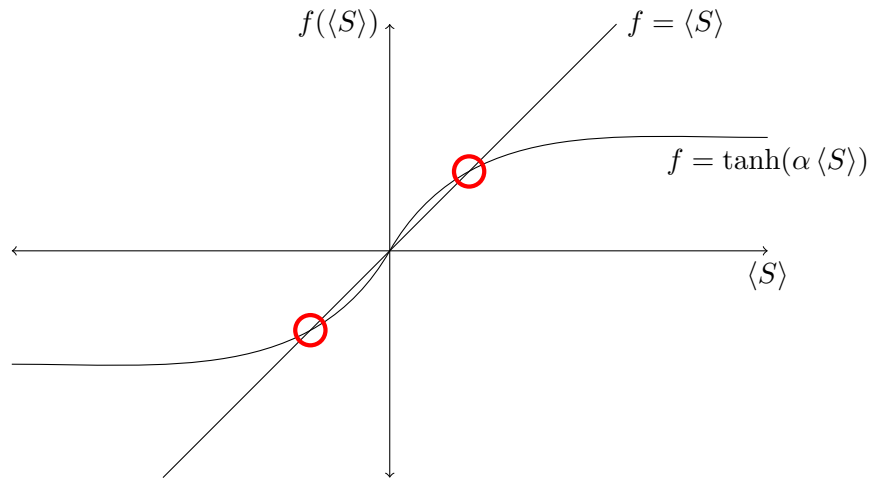
$$T_c = \frac{3J}{2k_B}.$$

Write the susceptibility in terms of this critical temperature.

$$\chi = \mu_0 n \frac{(g \mu_B)^2}{4k_B (T - T_c)}.$$

(e) Show graphically that in zero external field ($\mathbf{B} = 0$), below the critical temperature, there are solutions of the self consistency equation with $M \neq 0$.

The non-zero solutions are circled. Note that the zero solution remains, but is unstable.



We can even find these values near to T_c by expanding the tanh to third order.

9

Ground States

Consider the spin- $\frac{1}{2}$ Heisenberg Hamiltonian from the previous problem. Let us take \mathbf{B} to be in the $-\hat{z}$ direction, and assume a cubic lattice.

It will be useful to remember that

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2} (S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z.$$

(a) For $J > 0$, i.e, for the case of a ferromagnet, intuition tells us that the ground state of this Hamiltonian should simply have all spins aligned. Consider such a state. Show that this is an eigenstate of the Hamiltonian and find its energy.

So let's take all spins up,

$$|\psi\rangle = |\uparrow\rangle_1 \otimes |\uparrow\rangle_2 \otimes \dots \otimes |\uparrow\rangle_N$$

where $|\uparrow\rangle_i$ is the state defined specifically such that $S_i^z |\uparrow\rangle_i = |\uparrow\rangle_i$. Furthermore, $S_i^+ |\uparrow\rangle_i = 0$. Therefore,

$$\mathbf{S}_i \cdot \mathbf{S}_i |\psi\rangle = S_i^z S_i^z |\psi\rangle$$

only and so

$$H|\psi\rangle = -\frac{J}{2} \sum_{\langle i,j \rangle} |\psi\rangle - g\mu_B B \sum_i |\psi\rangle.$$

So, indeed, $|\psi\rangle$ is an eigenstate with energy

$$E = -\frac{J}{2} 6N - g\mu_B B N.$$

(b) For $J < 0$, the case of an antiferromagnet, one might expect that, at least for $\mathbf{B} = 0$, the state where spins on alternating sites point in opposite directions might be an eigenstate. Show that, in fact, this state is not an eigenstate of the Hamiltonian. Can you identify a state that is?

Let's take the (wrong) ansatz and see what it gives. Instead of writing down the state let's think about what $\mathbf{S}_i \cdot \mathbf{S}_j$ might do to any bond over which the spin flips.

$$\begin{aligned} \mathbf{S}_i \cdot \mathbf{S}_j |\uparrow\downarrow\rangle &= \frac{1}{2} S_i^- S_j^+ |\uparrow\downarrow\rangle + S_i^z S_j^z |\uparrow\downarrow\rangle \\ &= \frac{1}{2} |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle. \end{aligned}$$

So this cannot be an eigenstate because the spins on i and j have been flipped by the Hamiltonian.

We need to form singlet states instead. Note that

$$|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

is an eigenstate of $\mathbf{S}_i \cdot \mathbf{S}_j$ with eigenvalue of $\frac{1}{2}$. Therefore, we form a state in which the bonds alternate in this singlet pattern, namely

$$|\psi\rangle = \left| \begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow \\ \downarrow & \uparrow & \downarrow & \uparrow \\ \uparrow & \downarrow & \uparrow & \downarrow \\ \downarrow & \uparrow & \downarrow & \uparrow \end{array} \right\rangle - \left| \begin{array}{cccc} \downarrow & \uparrow & \downarrow & \uparrow \\ \uparrow & \downarrow & \uparrow & \downarrow \\ \downarrow & \uparrow & \downarrow & \uparrow \\ \uparrow & \downarrow & \uparrow & \downarrow \end{array} \right\rangle.$$

Whenever $\mathbf{S}_i \cdot \mathbf{S}_j$ acts on this it simply picks up $\frac{1}{2}$ because every bond taken individually is in a singlet state. Therefore, the total energy is

$$E = \frac{|J|}{2} \frac{6N}{2}$$

when $B = 0$ (note that this may well not be the ground state though. I'm not sure it is).