Solutions for Introduction to Graphene and Carbon Nanotubes 1st Edition by Proctor

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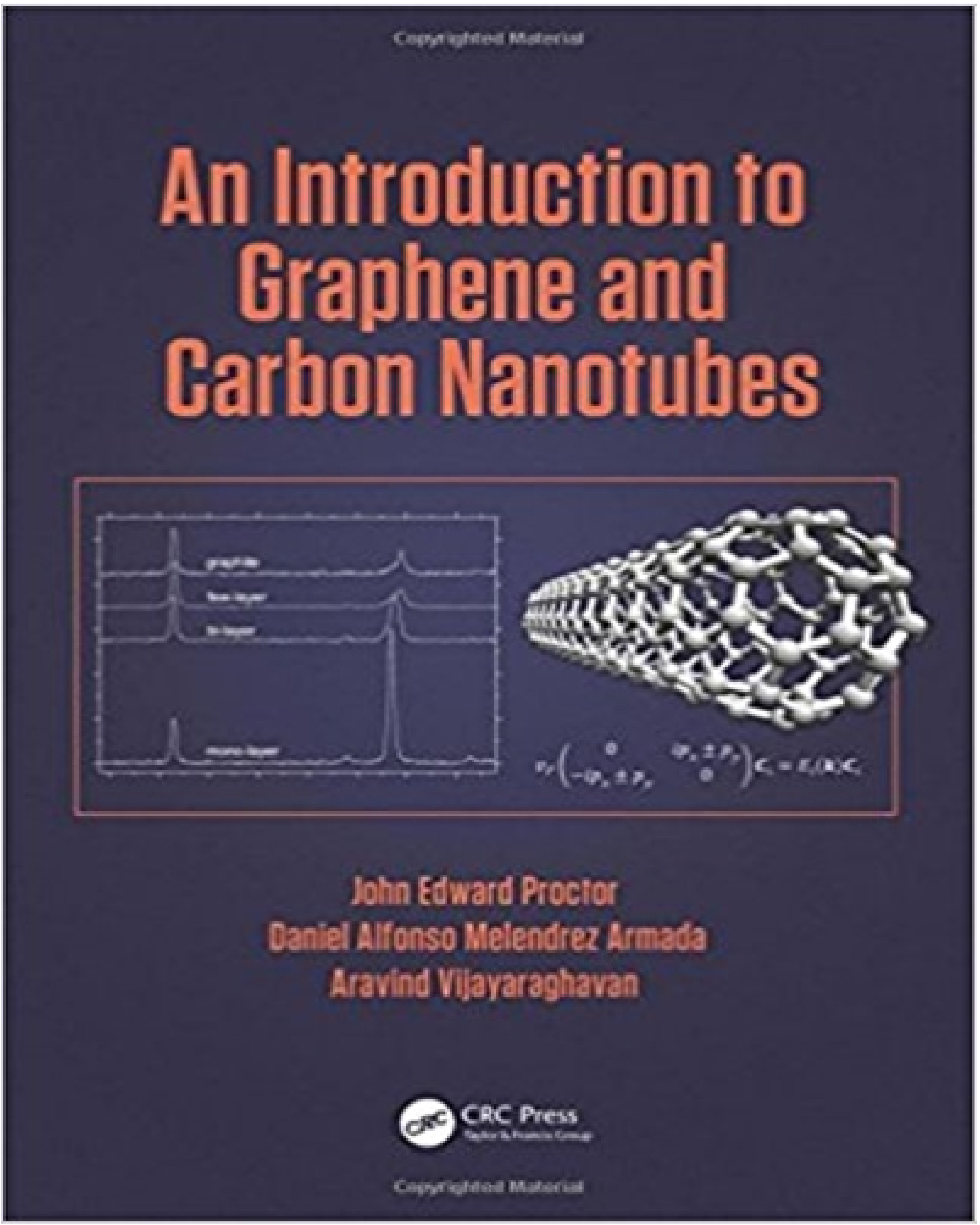


Solutions

Chapter 2

2.1 Orthonormality of sp-hybridized wavefunctions (easy)

The sp-hybridized wavefunctions for the carbon atom are as follows (combining equations 2.5 and 2.6 from the main text)):

$$\Psi(sp)_a = \frac{1}{\sqrt{2}}[\Psi(2s) + \Psi(2p_x)]$$

$$\Psi(sp)_b = \frac{1}{\sqrt{2}}[\Psi(2s) - \Psi(2p_x)]$$

Prove that these two wavefunctions are orthonormal (normalized and orthogonal). You may assume that the unhybridized wavefunctions $\Psi(2s)$ and $\Psi(2p_x)$ are orthonormal.

Solution: First we can verify that $\Psi(sp)_a$ is normalized. The condition for this is as follows:

$$\int |\Psi(sp)_a|^2 \, d\tau = 1$$

We evaluate this integral using the expression above for $\Psi(sp)_a$:

$$\int |\Psi(sp)_a|^2 \, d\tau = \frac{1}{2}\int [\Psi(2s) + \Psi(2p_x)]\,[\Psi^*(2s) + \Psi^*(2p_x)]d\tau$$

When these brackets are multiplied out, the only terms which will not integrate to zero are those where we multiply a wavefunction by its own complex conjugate (because $\Psi(2s)$ and $\Psi(2p_x)$ are orthogonal). Hence:

$$\int |\Psi(sp)_a|^2 \, d\tau = \frac{1}{2}\int \Psi(2s)\,\Psi^*(2s)d\tau + \frac{1}{2}\int \Psi(2p_x)\,\Psi^*(2p_x)d\tau$$

Since $\Psi(2s)$ and $\Psi(2p_x)$ are also both normalized, each of the integrals on the RHS is equal 1 and:

$$\int |\Psi(sp)_a|^2 \, d\tau = 1$$

As required. The same procedure demonstrates that $\Psi(sp)_b$ is normalized.

Next we can check that $\Psi(sp)_a$ and $\Psi(sp)_b$ are orthogonal. This condition can be written mathematically as follows:

$$\int \Psi(sp)_a \Psi^*(sp)_b d\tau = 0$$

Substituting for the hybridized wavefunctions gives:

$$\int \Psi(sp)_a \Psi^*(sp)_b d\tau = \frac{1}{2}\int [\Psi(2s) + \Psi(2p_x)]\,[\Psi^*(2s) - \Psi^*(2p_x)] d\tau$$

When these brackets are multiplied out, the only terms which will not integrate to zero are those where we multiply a wavefunction by its own complex conjugate (because $\Psi(2s)$ and $\Psi(2p_x)$ are orthogonal). Hence:

$$\int \Psi(sp)_a \Psi^*(sp)_b d\tau = \frac{1}{2}\int \Psi(2s)\,\Psi^*(2s) d\tau - \frac{1}{2}\int \Psi(2p_x)\,\Psi^*(2p_x) d\tau$$

Since $\Psi(2s)$ and $\Psi(2p_x)$ are also both normalized, each of the integrals on the right hand side is equal to 1 and:

$$\int \Psi(sp)_a \Psi^*(sp)_b d\tau = 0$$

As required.

2.2 Orthonormality of sp^2-hybridized wavefunctions (moderate)

The sp^2-hybridized wavefunctions for the carbon atom are as follows (combining equations 2.7 and 2.8 from the main text):

$$\Psi(sp^2)_a = \frac{1}{\sqrt{3}}\Psi(2s) - \sqrt{\frac{2}{3}}\Psi(2p_y)$$

$$\Psi(sp^2)_b = \frac{1}{\sqrt{3}}\Psi(2s) + \sqrt{\frac{2}{3}}\left[\frac{\sqrt{3}}{2}\Psi(2p_x) + \frac{1}{2}\Psi(2p_y)\right]$$

Prove that $\Psi(sp^2)_b$ is normalized and that $\Psi(sp^2)_a$ and $\Psi(sp^2)_b$ are orthogonal. You may assume that the unhybridized wavefunctions $\Psi(2s)$, $\Psi(2p_x)$ and $\Psi(2p_y)$ are orthonormal.

Solution: The normalization condition is that:

$$\int \Psi(sp^2)_b \Psi^*(sp^2)_b d\tau = 1$$

Which can be demonstrated as follows.

$$\Psi(sp^2)_b = \frac{1}{\sqrt{3}}\Psi(2s) + \frac{1}{\sqrt{2}}\Psi(2p_x) + \frac{1}{\sqrt{6}}\Psi(2p_y)$$

$$\int \Psi(sp^2)_b \Psi^*(sp^2)_b d\tau$$

$$= \int \left(\frac{1}{\sqrt{3}}\Psi(2s) + \frac{1}{\sqrt{2}}\Psi(2p_x) + \frac{1}{\sqrt{6}}\Psi(2p_y)\right)\left(\frac{1}{\sqrt{3}}\Psi^*(2s) + \frac{1}{\sqrt{2}}\Psi^*(2p_x) + \frac{1}{\sqrt{6}}\Psi^*(2p_y)\right) d\tau$$

When the brackets in the above expression are multiplied out, the only terms which will not integrate to zero are those where we multiply a wavefunction by its own complex conjugate. We therefore obtain:

$$\int \Psi(sp^2)_b \Psi^*(sp^2)_b d\tau = \frac{1}{3}\int \Psi(2s)\,\Psi^*(2s) d\tau + \frac{1}{2}\int \Psi(2p_x)\Psi^*(2p_x) d\tau + \frac{1}{6}\int \Psi(2p_y)\Psi^*(2p_y) d\tau$$

Each of the individual integrals on the right hand side of the above expression is equal to one, resulting in:

$$\int \Psi(sp^2)_b \Psi^*(sp^2)_b d\tau = \frac{1}{3} + \frac{1}{2} + \frac{1}{6} = 1$$

As required.

The condition for the $\Psi(sp^2)_a$ and $\Psi(sp^2)_b$ wavefunctions to be orthogonal is:

$$\int \Psi(sp^2)_a \Psi^*(sp^2)_b d\tau = 0$$

This can be proved as follows.

$$\int \Psi(sp^2)_a\Psi^*(sp^2)_b d\tau$$

$$= \int\left(\frac{1}{\sqrt{3}}\Psi(2s) - \sqrt{\frac{2}{3}}\Psi(2p_y)\right)\left(\frac{1}{\sqrt{3}}\Psi^*(2s) + \frac{1}{\sqrt{2}}\Psi^*(2p_x)\right.$$

$$\left. + \frac{1}{\sqrt{6}}\Psi^*(2p_y)\right)d\tau$$

As usual, when the brackets are multiplied out in the integral on the right hand side, the only terms which will not integrate to zero are those where we multiply a wavefunction by its own complex conjugate. Hence,

$$\int \Psi(sp^2)_a\Psi^*(sp^2)_b d\tau = \frac{1}{3}\int \Psi(2s)\Psi^*(2s)d\tau - \frac{1}{3}\int \Psi(2p_y)\Psi^*(2p_y)d\tau = 0$$

2.3 Hybridized wavefunctions for the non-identical atoms in the diamond lattice primitive unit cell (moderate)

In equation 2.10 in the main text (reproduced as equation 3 below) we wrote down expressions for the hybridized wavefunctions for sp^3-bonded carbon:

$$\Psi(sp^3)_a = \frac{1}{2}\left[\Psi(2s) + \Psi(2p_x) + \Psi(2p_y) + \Psi(2p_z)\right] \qquad (3)$$

$$\Psi(sp^3)_b = \frac{1}{2}\left[\Psi(2s) - \Psi(2p_x) - \Psi(2p_y) + \Psi(2p_z)\right]$$

$$\Psi(sp^3)_c = \frac{1}{2}\left[\Psi(2s) - \Psi(2p_x) + \Psi(2p_y) - \Psi(2p_z)\right]$$

$$\Psi(sp^3)_d = \frac{1}{2}\left[\Psi(2s) + \Psi(2p_x) - \Psi(2p_y) - \Psi(2p_z)\right]$$

However in diamond (just as in graphene) there are two atoms in the primitive unit cell, as illustrated in figure 1 below. We call these atoms A and B. Equation 3 above gives the hybridized wavefunctions for the A atom. Write down the hybridized wavefunctions (equivalent of equation 3) for the B atom.

Solution: To solve this problem it is necessary to relate the expressions for the wavefunctions (equation 3) to the directions in which the inter-atomic bonds point. If we, for instance, add the

$\Psi(2p_x)$ wavefunction (positive along the positive x-axis) to the $\Psi(2s)$ wavefunction (positive and spherically symmetric) we get a wavefunction which is large along the positive x-axis where we are adding one positive wavefunction to another. Considering this for the B atom we obtain:

$$\Psi(sp^3)_a = \tfrac{1}{2}\left[\Psi(2s) - \Psi(2p_x) - \Psi\left(2p_y\right) - \Psi(2p_z)\right]$$

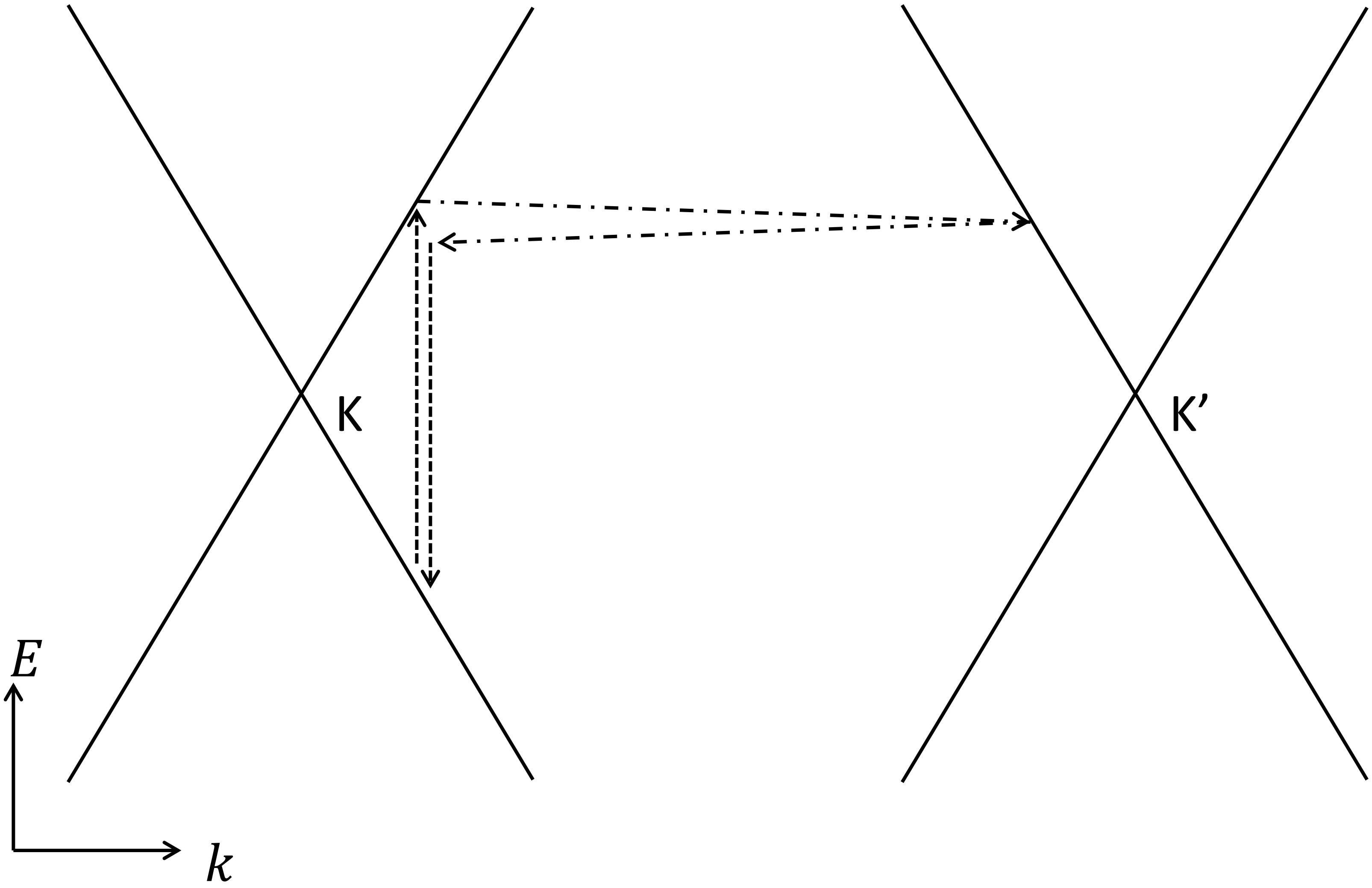
$$\Psi(sp^3)_b = \frac{1}{2}\left[\Psi(2s) - \Psi(2p_x) + \Psi\left(2p_y\right) + \Psi(2p_z)\right]$$

$$\Psi(sp^3)_c = \frac{1}{2}\left[\Psi(2s) + \Psi(2p_x) - \Psi\left(2p_y\right) + \Psi(2p_z)\right]$$

$$\Psi(sp^3)_d = \frac{1}{2}\left[\Psi(2s) + \Psi(2p_x) + \Psi\left(2p_y\right) - \Psi(2p_z)\right]$$

Comment for instructors: It would be possible to set many more problems on this topic. For instance, proving that any of the six sp^2 hybridized orbitals are normalized (equations 2.7 – 2.9), and that any combination of them for the same atom is orthogonal. This can also be done for the sp^3 orbitals for the A atom (equation 3) or the B atom (solution to problem 2.3

Instructors may find it useful to ask students to sketch the graphene lattice with the various electron wavefunctions marked on (reproducing figure 2.7 in the main text). This can be done as part of a class, and can lead to a discussion about what role the electrons with the different wavefunctions play – which electrons are responsible for graphene's conductivity and which are responsible for the strength of the inter-atomic bonds.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