Part 8. References

The following references were used to prepare aspects of these notes. They are recommended for those who wish to explore these topics in greater depth.

Quantum Transport

S. Datta, *Electronic Transport in Mesocopic Systems*.
Cambridge University Press 1995

S. Datta, *Quantum Transport: Atom to Transistor*.
Cambridge University Press 2005

Quantum Mechanics

P.L. Hagelstein, S.D. Senturia, and T.P. Orlando, *Introductory Applied Quantum and Statistical Mechanics*. Wiley 2004

P.W. Atkins and R.S. Friedman, *Molecular Quantum Mechanics*.
Oxford University Press, 3rd edition 1997

Ballistic Transistors

M. Lundstrom and J. Guo, *Nanoscale Transistors: Physics, Modeling, and Simulation*, Springer 2006.

Conventional MOS transistors

Y. Tsividis, *The MOS Transistor*.
Oxford University Press, 2nd edition 1999

Theory of computation

R. Feynman, *Lectures on Computation*.
Editors A.J.G. Hey and R.W. Allen, Addison-Wesley 1996

Appendix 1. Electron Wavepacket Propagation

Stationary states and eigenfunctions

Until now, we have not considered the velocity of electrons because we have not considered the time dependence of solutions to the Schrödinger equation. In Part 1, we broke the full Schrödinger Equation into two coupled equations: an equation in time, and another in space. The separation is possible when the potential energy is constant in time. Then the spatial and time dependencies of the solution can be separated, i.e.

$$\Psi(x,t) = \psi(x)\zeta(t) \tag{A.1.1}$$

The time dependence is described by:

$$E\zeta(t) = i\hbar\frac{d}{dt}\zeta(t) \tag{A.1.2}$$

and the spatial dependence is given by

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x). \tag{A.1.3}$$

Solutions to these coupled equations are characterized by a time-independent probability density. The general solution to Eq. (A.1.2) is

$$\zeta(t) = \zeta(0)\exp\left[-i\frac{E}{\hbar}t\right] \tag{A.1.4}$$

and the probability density is:

$$\left|\Psi(x,t)\right|^2 = \left|\psi(x)\zeta(t)\right|^2 = \left|\psi(x)\right|^2\left|\zeta(0)\right|^2 \tag{A.1.5}$$

Because the solution does not evolve with time, it is said to be 'stationary'. These solutions are important and are known as 'eigenfunctions'. Eigenfunctions are extremely important in quantum mechanics. You can think of them as the natural functions for a particular system. Each eigenfunction is associated with a constant, known as the eigenvalue: in this case the constant energy, E.

An arbitrary wavefunction, however, will not necessarily be an eigenfunction or stationary. For example, consider a wavefunction constructed from two eigenfunctions:

$$\left|\psi(x)\right\rangle = a_1\left|\psi_1(x)\right\rangle + a_2\left|\psi_2(x)\right\rangle \tag{A.1.6}$$

where a and b are constants. This is known as a linear combination of eigenfunctions. The full solution is

$$\Psi(x,t) = a_1\psi_1(x)e^{-i\frac{E_1}{\hbar}t} + a_2\psi_2(x)e^{-i\frac{E_2}{\hbar}t} \tag{A.1.7}$$

Substituting into the Schrödinger Equation gives

$$H\left|a_1\psi_1(x)e^{-i\frac{E_1}{\hbar}t} + a_2\psi_2(x)e^{-i\frac{E_2}{\hbar}t}\right\rangle = a_1E_1\left|\psi_1(x)e^{-i\frac{E_1}{\hbar}t}\right\rangle + a_2E_2\left|\psi_2(x)e^{-i\frac{E_2}{\hbar}t}\right\rangle \tag{A.1.8}$$

i.e., the linear combination is not necessarily itself an eigenfunction. It is not stationary: the phase of each eigenfunction component evolves at a different rate. The probability

Appendix 1. Electron Wavepacket Propagation

density shows time dependent interference between each rotating phase term. For example, assuming that a_1, a_2, ψ_1 and ψ_2 are real:

$$\left|\Psi(x,t)\right|^2 = a_1^2 \psi_1^2(x) + a_2^2 \psi_2^2(x) + 2a_1 a_2 \psi_1(x)\psi_2(x)\cos\left((E_2 - E_1)\frac{t}{\hbar}\right). \quad (A.1.9)$$

Completeness

We will not prove completeness in the class. Instead we merely state that the completeness property of eigenfunctions allows us to express any well-behaved function in terms of a linear combination of eigenfunctions. i.e. if $|\phi_n\rangle$ is an eigenfunction, then an arbitrary well-behaved wavefunction can be written

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle \quad (A.1.10)$$

Completeness also requires that the potential be finite within the region of interest. For example, no combination of eigenfunctions of the infinite square well can ever describe a non-zero wavefunction amplitude at the walls.

Re-expressing the wavefunction in terms of a weighted sum of eigenfunctions is a little like doing a Fourier transform, except that instead of re-expressing the wavefunction in terms of a linear combination of exp[ikx] factors, we are using the eigenfunctions.[†]

The problem now is the determination of the weighting constants, a_n.

For this we need the next property of eigenfunctions:

Orthogonality

Eigenfunctions with different eigenvalues are orthogonal. *i.e.* the bracket of eigenfunctions corresponding to different eigenvalues is zero:

$$\langle\phi_j|\phi_i\rangle = 0, \quad for \quad i \neq j, \quad E_i \neq E_j \quad (A.1.11)$$

If different eigenfunctions have identical eigenvalues (*i.e.* same energy) they are known as *degenerate*.

Calculation of coefficients

Starting from Eq. (A.1.10) we have

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle \quad (A.1.12)$$

Now, let's take the bracket with an eigenfunction $\langle\phi_k|$

$$\langle\phi_k|\psi\rangle = \langle\phi_k|\sum_n a_n|\phi_n\rangle = \sum_n a_n\langle\phi_k|\phi_n\rangle \quad (A.1.13)$$

From the statement of orthogonality in Eq. (A.1.11) we have

[†] Note that exp[ikx] provides a continuous set of eigenfunctions for unbound states, i.e., the expansion in terms of eigenfunctions is the Fourier transform.

$$\langle \phi_k | \phi_n \rangle = \delta_{nk} \tag{A.1.14}$$

where δ_{nk} is the Kronecker delta function, i.e. $\delta_{nk} = 1$ only when $n = k$.

Thus,

$$a_k = \langle \phi_k | \psi \rangle. \tag{A.1.15}$$

These coefficients are very important.

Since the eigenfunctions are usually known, often the set of coefficients provides the interesting information in a particular problem. This may be clear from an example.

An example: the expanding square well

Consider an electron occupying the ground state of an infinite square well of length L. As shown in Fig. A 1.1, at time $t = 0$, the well suddenly triples in size. What happens to the electron?
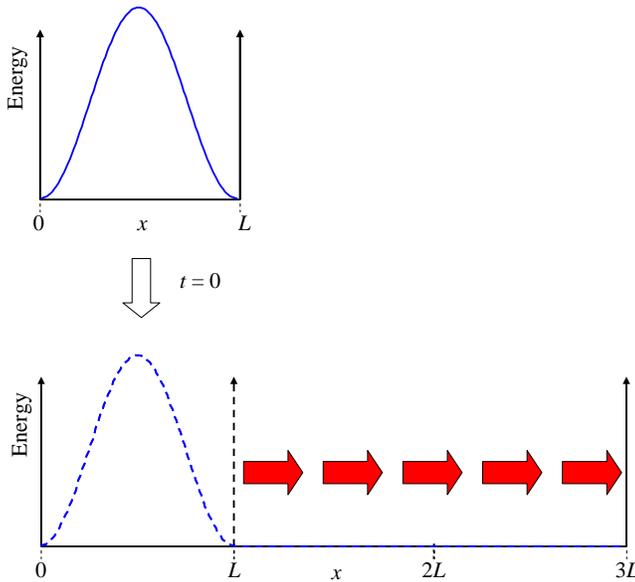

Fig. A 1.1. An electron is in the ground state of an infinite potential well. Suddenly the infinite well expands instantaneously to three times its previous size.

Let's begin to answer this question by considering the wavefunction prior to the expansion of the well:[†]

$$\psi(x) = \sqrt{\frac{2}{L}} \sin(\pi x/L), \quad 0 \le x \le L \tag{A.1.16}$$

If we substitute this back into the Schrödinger Equation we can easily confirm that the effect of operating on this wavefunction with the Hamiltonian is the same as multiplying the wavefunction by a constant. i.e.

$$H \left| \sqrt{\frac{2}{L}} \sin(\pi x/L) \right\rangle = E \left| \sqrt{\frac{2}{L}} \sin(\pi x/L) \right\rangle \tag{A.1.17}$$

[†] Note that relative the previous square well analysis (see Fig. 1.21) we have shifted the x-axis here such that the left wall is at $x = 0$.

Appendix 1. Electron Wavepacket Propagation

Thus, this wavefunction is an *eigenfunction* of the original square well, and the constant, *E*, the energy, is the *eigenvalue* corresponding to the eigenfunction.

Now, Eq. (A.1.16) is the lowest energy eigenfunction for the time independent infinite square well potential. The wavefunction evolves in time according to

$$E\zeta(t) = i\hbar \frac{d}{dt}\zeta(t) \tag{A.1.18}$$

Solving Eq. (A.1.2) gives:

$$\Psi(x,t) = \psi(x)\zeta(t) = \sqrt{\frac{2}{L}}\sin(\pi x/L)\exp\left[-i\frac{E}{\hbar}t\right] \tag{A.1.19}$$

where

$$E = E_L = \frac{\hbar^2 \pi^2}{2mL^2}. \tag{A.1.20}$$

The probability density, however, is time independent:

$$|\Psi(x,t)|^2 = \frac{2}{L}\sin^2(\pi x/L), \quad 0 \le x \le L \tag{A.1.21}$$

We have verified that the eigenfunction is stationary, as it must be.

Now, when the well expands, the wavefunction cannot change instantaneously. To confirm this, consider a step change in the wavefunction in Eq. (A.1.2) – the energy would tend to ∞.

But the stationary states of the new well are

$$\psi(x) = \sqrt{\frac{2}{3L}}\sin(n\pi x/3L), \quad 0 \le x \le 3L \tag{A.1.22}$$

i.e. the wavefunction of the electron at *t* = 0 is not a stationary state in the expanded well. *To determine the evolution of the electron wavefunction in time, we must re-express the wavefunction in terms of the eigenfunctions of the expanded well.* We can then calculate the evolution of each eigenfunction from Eq. (A.1.2).

The wavefunction is now described as a *linear combination* of eigenfunctions:

$$\psi(x) = \sqrt{\frac{2}{L}}\sin(\pi x/L), \quad 0 \le x \le L$$
$$= \sum_n a_n \sqrt{\frac{2}{3L}}\sin(n\pi x/3L), \quad 0 \le x \le 3L \tag{A.1.23}$$

where a_n is a set of constants, that weight the contributions from each eigenfunction.

We express the wavefunction as a linear combination of the eigenfunctions of the *expanded* well. From Eq. (A.1.15) we have

$$\psi(x) = \sum_n a_n \sqrt{\frac{2}{3L}}\sin(n\pi x/3L), \quad 0 \le x \le 3L \tag{A.1.24}$$

Thus, the coefficients are

$$a_n = \langle \phi_n | \psi \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\pi x/L\right) \sqrt{\frac{2}{3L}} \sin\left(n\pi x/3L\right) dx \qquad \text{(A.1.25)}$$

Solving gives

$$a_n = \begin{cases} \dfrac{1}{\sqrt{3}} & n = 3 \\[2ex] -\dfrac{6\sqrt{3}}{\pi} \dfrac{\sin\left(n\pi/3\right)}{n^2 - 9} & n \neq 3 \end{cases} \qquad \text{(A.1.26)}$$

In Fig. A 1.2 we plot the cumulative effect of adding the weighted eigenfunctions. After about 10 eigenfunctions, the linear combination is a close approximation to the initial wavefunction.
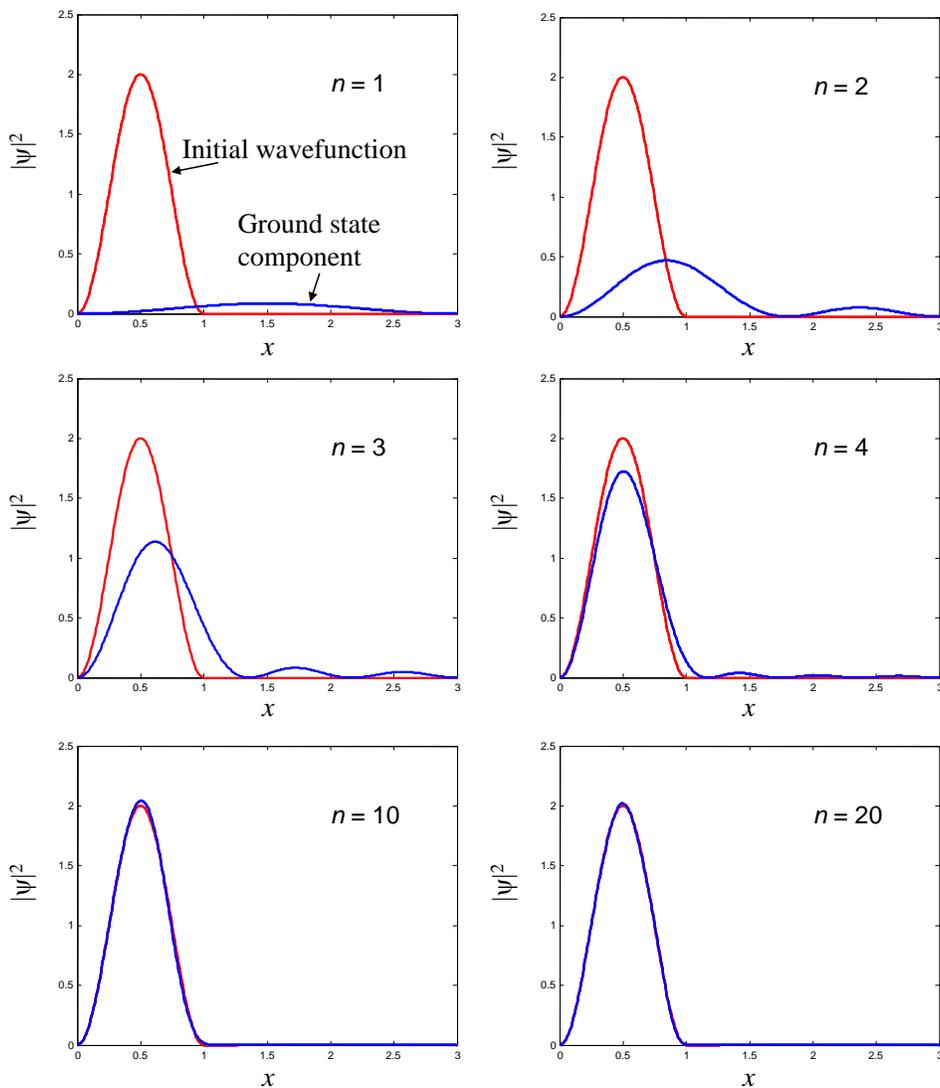
Fig. A 1.2. Here we show various approximations for the initial wavefunction. We need about 10 weighted eigenfunctions for a close match. The agreement gets better with addition eigenfunctions.

Appendix 1. Electron Wavepacket Propagation

Next, we calculate the evolution of the wavefunction. From Eq. (A.1.24), we get

$$\Psi(x,t) = \sum_n a_n \sqrt{\frac{2}{3L}} \sin(n\pi x/3L) \exp\left[-i\frac{E_n}{\hbar}t\right], \quad 0 \le x \le 3L \qquad \text{(A.1.27)}$$

where

$$E_n = \frac{n^2\pi^2\hbar^2}{2m(3L)^2} \qquad \text{(A.1.28)}$$

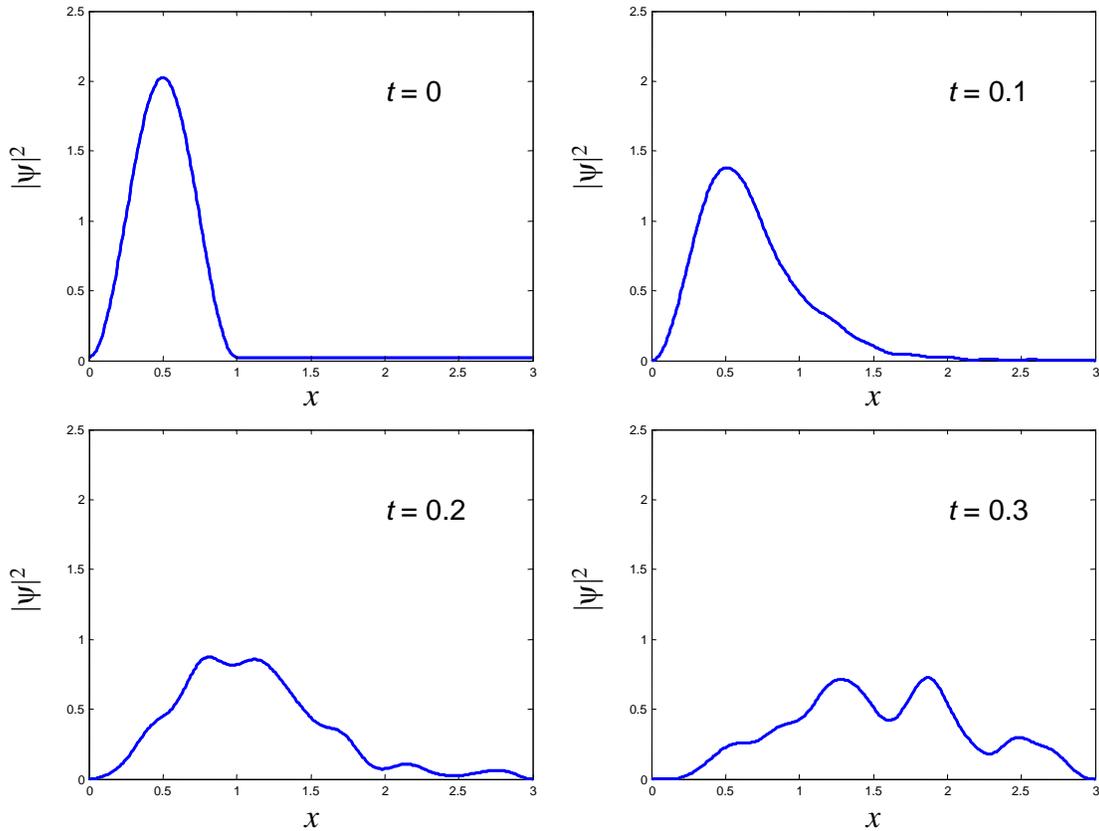The evolution of the wavefunction with time is shown in Fig. A 1.3, below.

Fig. A 1.3. The evolution of the wavefunction after the expansion of the walls at $t = 0$.

Propagation of a Gaussian Wavepacket

Next we will examine the propagation of a Gaussian wavepacket in free space. Again, we will expand the wavefunction in terms of its eigenfunctions.

Consider an electron in free space. Let the initial wavepacket be a Gaussian.

$$\psi(x,0) = \left(\pi L^2\right)^{-1/4} \exp\left[-\frac{x^2}{2L^2}\right] \exp[ik_0 x] \tag{A.1.29}$$

Note that we have introduced a phase factor $\exp[ik_0 x]$. Recall that multiplying the real space wavefunction by the phase factor $\exp[ik_0 x]$, is equivalent to shifting the k-space wavefunction by k_0. Since the Fourier transform was centered at $k = 0$ prior to the shift, the phase factor shifts the expectation value of k to k_0. Hence the factor $\exp[ik_0 x]$ gives the wavepacket has a non-zero average momentum.

Now, the eigenfunctions of the Schrödinger Equation in free space are the complex exponentials

$$\phi(k) = \exp[ikx] \tag{A.1.30}$$

where k is continuous.

Each eigenfunction evolves with time as

$$\phi(k,t) = \exp[ikx] \exp\left[-i\frac{E}{\hbar}t\right] \tag{A.1.31}$$

Expanding the wavefunction as a linear combination of these eigenfunctions we have

$$\psi(x,t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} A(k)\phi(k,t)dk \tag{A.1.32}$$

$$\psi(x,t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} A(k)\exp[ikx]\exp\left[-i\frac{E}{\hbar}t\right]dk \tag{A.1.33}$$

where $A(k)/2\pi$ describes the weighting of each complex exponential eigenfunction.

Since $\phi(k) = \exp[ikx]$, Eq. (A.1.32) evaluated at $t = 0$ is simply the inverse Fourier transform:

$$\psi(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} A(k)\exp[ikx]dk \tag{A.1.34}$$

Thus, $A(k)$ is determined from the Fourier transform of the wavefunction

$$A(k) = \langle \phi(k)|\psi(x,0)\rangle = \int_{-\infty}^{+\infty} \psi(x,0)e^{-ikx}dx = \left(4\pi L^2\right)^{1/4} \exp\left[-\frac{L^2(k-k_0)^2}{2}\right] \tag{A.1.35}$$

Now, before we can substitute $A(k)$ back into Eq. (A.1.32) to get the time evolution of $\psi(x,t)$ we need to consider the possible k dependence of energy, E.

In general the relation between E and k is known as the **dispersion relation**.

Appendix 1. Electron Wavepacket Propagation

The dispersion relation is important because propagation of an electron in free space, or in a particular material is determined by the dispersion relation. Let's consider some examples.

(i) Linear dispersion relation

The dispersion relation determines how the wavepacket spreads in time. For example, if instead of an electron we were considering a photon with $E = \hbar\omega = \hbar ck$, the dispersion relation is linear and the photon does not spread as it propagates.
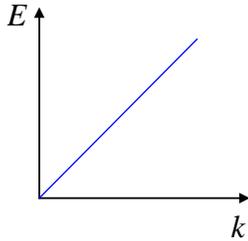
Fig. A 1.4. A linear dispersion relation.

The time dependent factor is

$$\exp\left[-i\frac{E}{\hbar}t\right] \equiv \exp[-i\omega t] = \exp[-ickt] \tag{A.1.36}$$

Solving Eq. (A.1.32) gives

$$\psi(x,t) = \frac{1}{\left(\pi L^2\right)^{1/4}} \exp\left[ik_0(x-ct)\right]\exp\left[-\frac{(x-ct)^2}{2L^2}\right]. \tag{A.1.37}$$

Thus, the probability density is simply the original function shifted linearly in time:

$$|\psi(x,t)|^2 = \frac{1}{\left(\pi L^2\right)^{1/2}} \exp\left[-\frac{(x-ct)^2}{L^2}\right] \tag{A.1.38}$$

(ii) Quadratic dispersion relation

For plane wave eigenfunctions, however, the dispersion relation is quadratic and we have
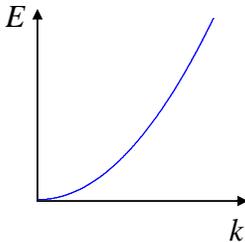
$$E = \frac{\hbar^2 k^2}{2m} \tag{1.39}$$

Fig. A 1.5. A quadratic dispersion relation.

As we have seen, particles in a box also have quadratic dispersion relations.

Thus the time dependent factor is

$$\exp\left[-i\frac{E}{\hbar}t\right] \equiv \exp[-i\omega t] = \exp\left[-i\frac{\hbar k^2}{2m}t\right] \quad \text{(A.1.40)}$$

Solving Eq. (A.1.32) gives

$$\psi(x,t) = \frac{1}{\left(\pi L^2\right)^{1/4}} \frac{1}{\sqrt{1+i\,\hbar t/mL^2}} \exp\left[i\left(k_0 x - \frac{\hbar k_0^2 t}{2m}\right)\right] \exp\left[-\frac{(x-\hbar k_0 t/m)^2}{2L^2\left(1+i\,\hbar t/mL^2\right)}\right] \text{(A.1.41)}$$
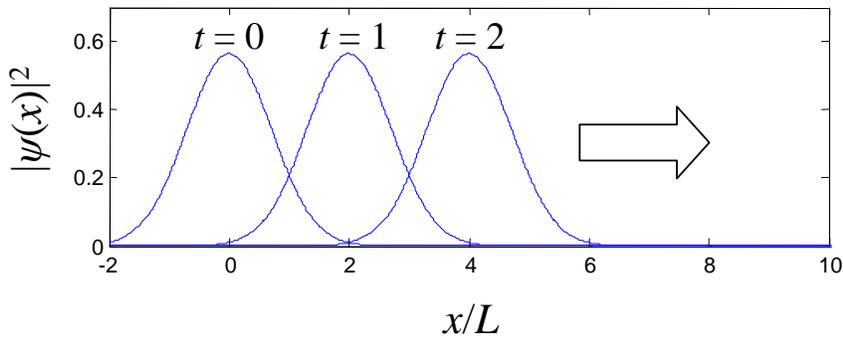
and

$$|\psi(x,t)|^2 = \left(2\pi\left[\Delta x(t)\right]^2\right)^{-1/2} \exp\left[-\frac{(x-\hbar k_0 t/m)^2}{2\left[\Delta x(t)\right]^2}\right] \quad \text{(A.1.42)}$$
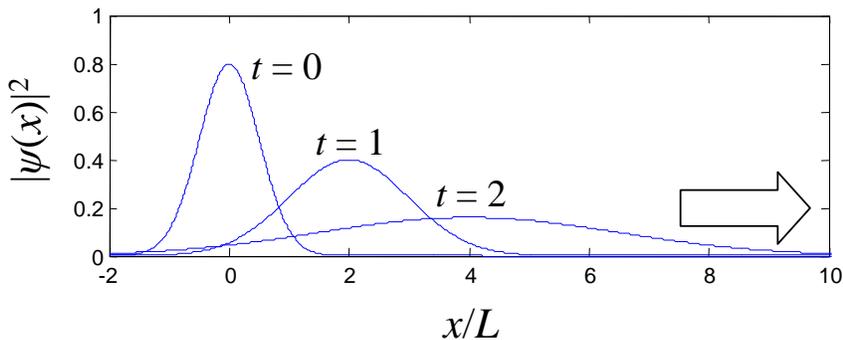
where

$$\left[\Delta x(t)\right]^2 = \frac{L^2}{2}\left(1+\left(\frac{\hbar t}{mL^2}\right)^2\right) \quad \text{(A.1.43)}$$

Propagation with linear dispersion relation

Propagation with quadratic dispersion relation

Appendix 1. Electron Wavepacket Propagation

Fig. A 1.6. The evolution of a Gaussian wavepacket for linear and quadratic dispersion relations.

Group Velocity

As with a classical wave, the average velocity of the wavepacket is the **group velocity**, defined as the time derivative of the expectation value of position:

$$v_g = \frac{d}{dt}\langle x \rangle = \left\langle \frac{1}{\hbar}\frac{dE}{dk}\right\rangle = \left\langle \frac{d\omega}{dk}\right\rangle \tag{A.1.44}$$

If the wavepacket is highly peaked in k-space it is possible to simplify Eq. (A.1.44) by evaluating $d\omega/dk$ at the expectation value of k:

$$v_g = \left\langle \frac{d\omega}{dk}\right\rangle \approx \frac{d\omega}{dk}\bigg|_{\langle k \rangle} \tag{A.1.45}$$

For the linear dispersion relation, $d\omega/dk$ is constant so we don't need the approximation:

$$v_g = \frac{d\omega}{dk} = c \tag{A.1.46}$$

i.e. the photon moves along at the speed of light, as expected.

For the quadratic dispersion relation, we have

$$v_g = \left\langle \frac{d\omega}{dk}\right\rangle = \left\langle \frac{\hbar k}{m}\right\rangle = \frac{\hbar k_0}{m} \tag{A.1.47}$$

Since $\hbar k_0$ is the expectation value of momentum, this is indeed the average velocity.

Problems

1. Consider the electron in the expanded well discussed in the notes. Numerically simulate the wave function as a function of time. Using the simulation or otherwise, determine the expectation value of energy before and after the well expands? Predict the behavior of the expectation values of position and momentum as a function of time.
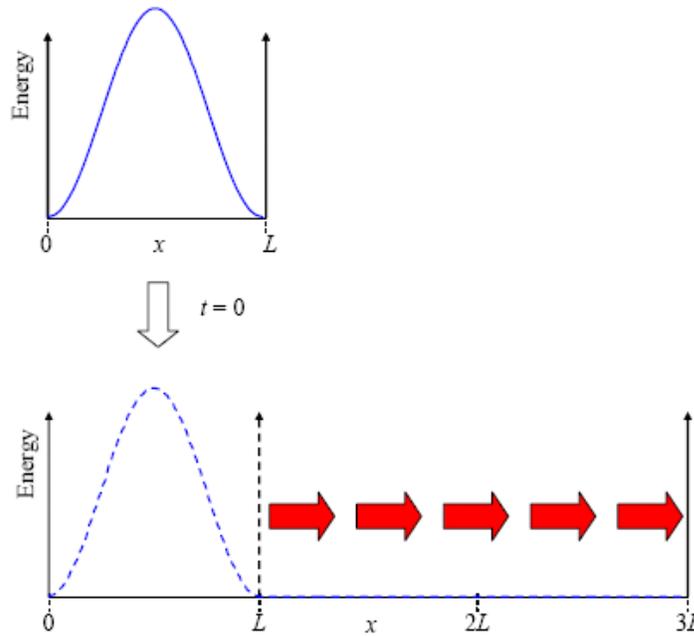

Fig. A 1.7. The expanding well.

2. Consider the wave function in an infinite square well of width L illustrated below at time $t = 0$. How will the wavefunction evolve for $t > 0$. Will the wave function ever return to its original position? If so, at what time $t = T$ will this occur?
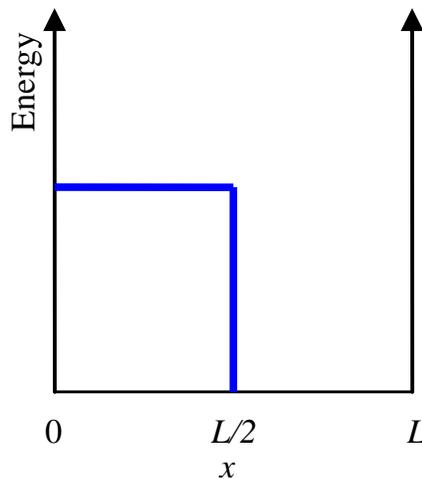

Fig. A 1.8. An initial state within a quantum well.

Appendix 1. Electron Wavepacket Propagation

3. Derive the expression for the propagation of a Gaussian wavepacket with the linear dispersion relation $E = \hbar\omega = \hbar ck$. (Equation (A.1.37))

Appendix 2. The hydrogen atom

The box model of the hydrogen atom

Hydrogen is the simplest element. There are just two components: an electron, and a positively charged nucleus comprised of a single proton.

Perhaps the simplest model of the hydrogen atom employs our now familiar square potential wells. This approximation cannot be taken very far, but it does illustrate the origin of the shapes of some of the orbitals.

If we compare the smooth, spherically symmetric Coulomb potential to our box model of an atom, it is clear that the box approximation will give up a lot of accuracy in the calculation of atomic orbitals and energy. The box, however, does yield insights into the shape of the various possible atomic orbitals.

The box is a separable potential. Thus, the atomic orbitals can be described by a product:

$$\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z) \tag{A.2.1}$$

If the wall have infinite potential, the possible energies of the electron are given by

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{A.2.2}$$

where the dimensions of the box are $L_x \times L_y \times L_z$ and n_x, n_y and n_z are integers that correspond to the state of the electron within the box.

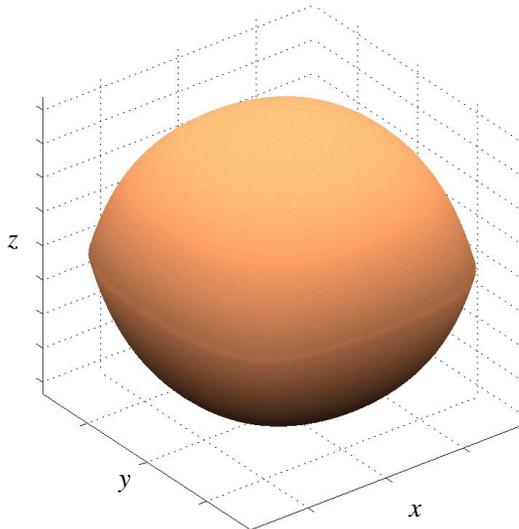For example, consider the ground state of a box with infinite potential walls. $(n_x, n_y, n_z) = (1,1,1)$

Fig. A 2.1. The ground state of a 3 dimensional box. $(n_x, n_y, n_z) = (1,1,1)$

Appendix 2. The hydrogen atom

Now, consider the orbital's shape if either $\psi_x(x)$ or $\psi_y(y)$ or $\psi_z(z)$ is in the first excited state: $(n_x,n_y,n_z) = (2,1,1)$, $(n_x,n_y,n_z) = (1,2,1)$ or $(n_x,n_y,n_z) = (1,1,2)$

The $1s$ orbital is similar to $(n_x,n_y,n_z) = (1,1,1)$. The p orbitals are similar to the first excited state of the box, i.e. $(n_x,n_y,n_z) = (2,1,1)$ is similar to a p_x orbital, $(n_x,n_y,n_z) = (1,2,1)$ is similar to a p_y orbital and $(n_x,n_y,n_z) = (1,1,2)$ is similar to a p_z orbital.
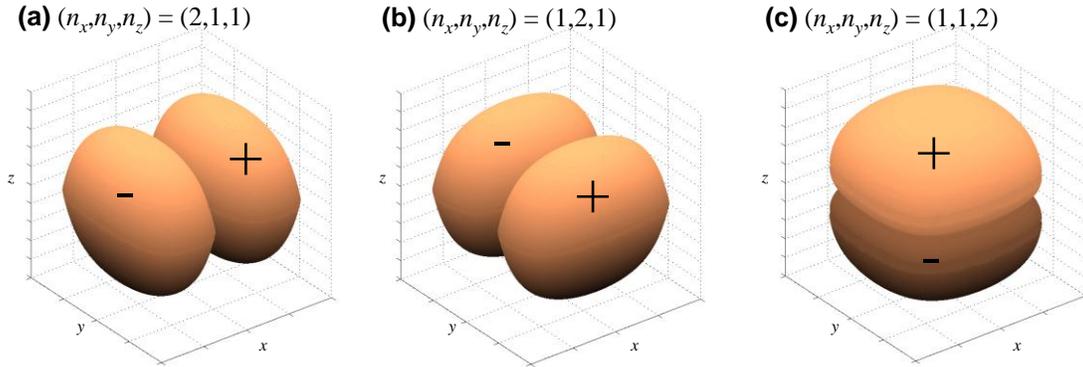

Fig. A 2.2. The first excited states of a 3 dimensional box. **(a)** $(n_x,n_y,n_z) = (2,1,1)$, **(b)** $(n_x,n_y,n_z) = (1,2,1)$, **(c)** $(n_x,n_y,n_z) = (1,1,2)$.

The approximation soon breaks down, however. The $2s$ orbital, which has the same energy as the $2p$ orbitals is most similar to the box orbital $(n_x,n_y,n_z) = (3,3,3)$, which has significantly higher energy. Nevertheless, the box does illustrate the alignment of the three p orbitals with the x, y and z axes.

Appendix 3. The Born-Oppenheimer approximation[†]

Consider the hydrogen atom Hamiltonian. Let the electron coordinate be x, and the nuclear coordinate be X. We will assume that the system is one dimensional for the purposes of explaining the approximation.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2} - \frac{\hbar^2}{2m_N}\frac{d^2}{dX^2} - \frac{e^2}{4\pi\varepsilon_0|x-X|} \tag{A.3.1}$$

Now let's separate the solution, ψ, into an electron-only factor φ, and the nuclear-dependent factor χ:

$$\psi(x,X) = \varphi(x,X)\chi(X). \tag{A.3.2}$$

Substituting into Eq. (A.3.1) gives:

$$H\psi = -\frac{\hbar^2}{2m_e}\frac{d^2\varphi}{dx^2}\chi - \frac{\hbar^2}{2m_N}\left(\frac{d^2\varphi}{dX^2}\chi + 2\frac{d\varphi}{dX}\frac{d\chi}{dX} + \frac{d^2\chi}{dX^2}\varphi\right) + V(x,X)\varphi\chi \tag{A.3.3}$$

where we have replaced the Coulomb potential by V.

Now using the Born-Oppenheimer approximation, *i.e.* $m_e \ll m_N$, we approximate Eq. (A.3.3) by:

$$H\psi = -\frac{\hbar^2}{2m_e}\frac{d^2\varphi}{dx^2}\chi + V(x,X)\varphi\chi. \tag{A.3.4}$$

Next, canceling the nuclear-dependent factor χ:

$$H\varphi = -\frac{\hbar^2}{2m_e}\frac{d^2\varphi}{dx^2} + V(x,X)\varphi. \tag{A.3.5}$$

This equation is used to solve for the electron coordinates in a given nuclear configuration. The nuclear configuration is then optimized.

[†] This Appendix is adapted in part from *Molecular Quantum Mechanics* by Atkins and Friedman

Appendix 4. Hybrid Orbitals

Linear alignment with two neighbors (sp hybridization)

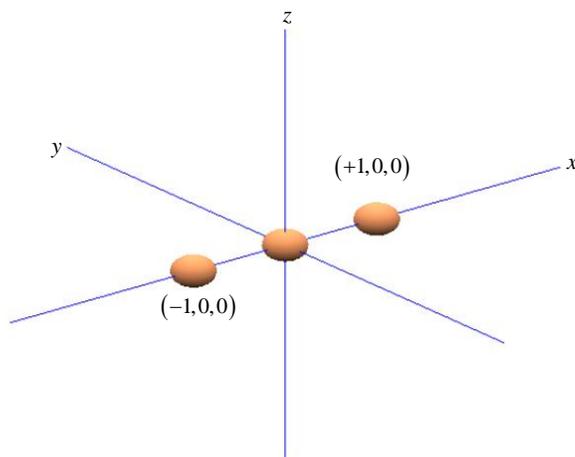Consider three atoms in a line, as shown in Fig. A 4.1. Arbitrarily we align the atoms with the *x*-axis.

Fig. A 4.1. Three atoms in a line.

We wish to determine the contribution of the central atom's orbitals to σ bonds. Recall that σ bonds have electron density on the axis between the atoms.

Now, if the basis set consists of *s* and *p* orbitals, only *s* and p_x orbitals can contribute to σ bonds on the *x*-axis. p_y and p_z orbitals have zero density on the *x*-axis and therefore cannot contribute to the σ bonds. They may contribute to π bonds however.

Let's define the symmetry adapted atomic orbitals that contribute to σ bonds generally as:

$$\phi_\sigma = c_s \phi_s + c_{p_z} \phi_{p_z} \tag{A.4.1}$$

where c_s and c_{px} are the weighting coefficients for the s and px orbitals respectively. There are two σ bonds: one to the left, and one to the right. We'll define the two symmetry adapted atomic orbitals that contribute to these σ bonds as ϕ_σ^1 and ϕ_σ^2 respectively.

The *s* orbital contributes equally to both symmetry adapted atomic orbitals. *i.e.*

$$|c_s|^2 = \frac{1}{2}, \quad c_s = \frac{1}{\sqrt{2}} \tag{A.4.2}$$

Since the p_x orbital is aligned with the *x*-axis, we can weight the p_x orbital components by the coordinates of the two neighboring atoms at $x = +1$ and $x = -1$,

$$\phi_\sigma^1 = c_s \phi_s + c_p \phi_{p_x}$$
$$\phi_\sigma^2 = c_s \phi_s - c_p \phi_{p_x}$$

(A.4.3)

In the first orbital, we are adding the *s* and p_x orbitals in-phase. Consequently, we have maximum electron density in the positive *x*-direction. In the second, we are adding the *s* and p_x orbitals out of phase, yielding a maximum electron density in the negative *x*-direction.

Normalizing each orbital gives

$$\left| c_p \right|^2 = \frac{1}{2}, \quad c_p = \sqrt{\frac{1}{2}}$$

(A.4.4)

Thus, the first symmetry adapted atomic orbital is

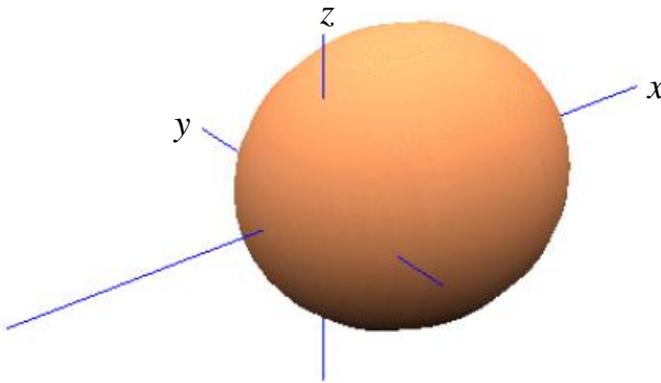$$\phi_\sigma^1 = \tfrac{1}{\sqrt{2}}\left(\phi_s + \phi_{p_x} \right)$$

(A.4.5)

Fig. A 4.2. The *sp* hybrid-ized atomic orbital in the *+x* direction.

Similarly, the second symmetry adapted atomic orbital is

$$\phi_\sigma^2 = \tfrac{1}{\sqrt{2}}\left(\phi_s - \phi_{p_x} \right).$$
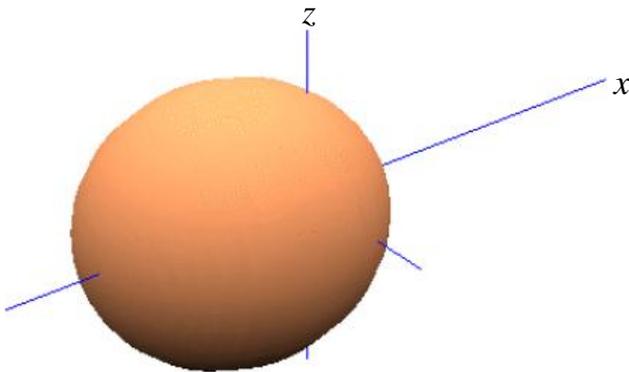
(A.4.6)

Fig. A 4.3. The *sp* hybrid-ized atomic orbital in the *−x* direction.

Thus, based purely on symmetry arguments, in a linear chain of atoms it is convenient to re-express the four atomic orbitals *s*, p_x, p_y and p_z, as

$$\phi_\sigma = \tfrac{1}{\sqrt{2}}\left(\phi_s \pm \phi_{p_x} \right),$$

(A.4.7)

Appendix 4. Hybrid Orbitals

where p_y and p_z remain unaffected. This is known as *sp* hybridization since we have combined one *s* atomic orbital, and one *p* atomic orbital to create two atomic orbitals that contribute to σ bonds.
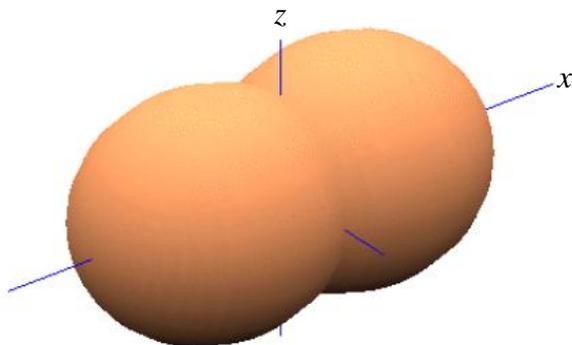

Fig. A 4.4. We plot both *sp* hybridized atomic orbitals. They point along the *x*-axis.

The remaining p_y and p_z atomic orbitals may combine in molecular orbitals with higher energy. The highest occupied molecular orbital (HOMO) is also known as the frontier molecular orbital. In an *sp*-hybridized material, the frontier molecular orbital will be a linear combination of p_y and p_z atomic orbitals. The frontier molecular orbital is relevant to us, because it more likely than deeper levels to be partially filled. Consequently, conduction is more likely to occur through the HOMO than deeper orbitals.

Now, σ bonds possess electron densities localized between atoms. But π bonds composed of linear combinations of *p* orbitals can be *delocalized* along a chain or sheet of atoms. Thus, if the HOMO is a π bond, it is much easier to push an electron through it; we'll see some examples of this in the next section.

Planar alignment with three neighbors (sp² hybridization)

Consider a central atom with three equispaced neighbors at the points of a triangle; as shown in Fig. A 4.5. Arbitrarily we align the atoms on the *x-y* plane.
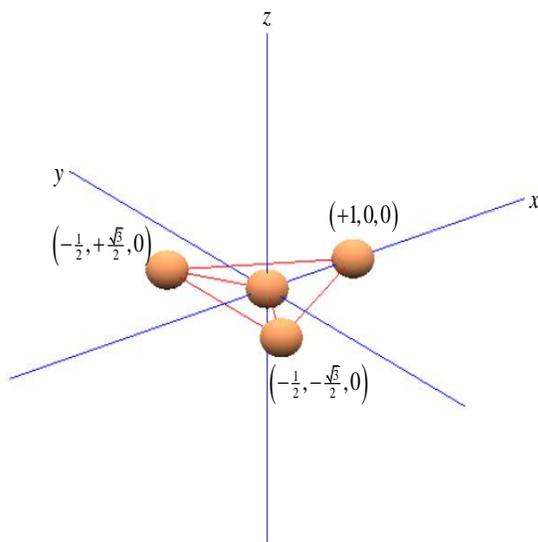

Fig. A 4.5. A central atom and its neighbors. Electrostatic repulsion can force the neighbors to the points of an equilateral triangle.

Once again, we wish to determine the contribution of the central atom's orbitals to σ bonds. If the basis set consists of s and p orbitals, only s, p_x and p_y atomic orbitals can contribute to σ bonds in the x-y plane. p_z orbitals can only contribute to π bonds.

Let's define the symmetry adapted atomic orbitals that contribute individually to σ bonds generally as:

$$\phi_\sigma = c_s \phi_s + c_{p_x} \phi_{p_x} + c_{p_y} \phi_{p_y} \tag{A.4.8}$$

The s orbital contributes equally to all three symmetry adapted atomic orbitals. i.e.

$$\left| c_s \right|^2 = \frac{1}{3}, \quad c_s = \frac{1}{\sqrt{3}} \tag{A.4.9}$$

Since the p_x orbital is aligned with the x-axis, and p_y with the y-axis, we can weight the p orbital components by the coordinates of the triangle of neighboring atoms

$$\phi_\sigma^1 = c_s \phi_s + c_p \left(+1\phi_{p_x} + 0\phi_{p_y} \right)$$

$$\phi_\sigma^2 = c_s \phi_s + c_p \left(-\tfrac{1}{2}\phi_{p_x} + \tfrac{\sqrt{3}}{2}\phi_{p_y} \right) \tag{A.4.10}$$

$$\phi_\sigma^3 = c_s \phi_s + c_p \left(-\tfrac{1}{2}\phi_{p_x} - \tfrac{\sqrt{3}}{2}\phi_{p_y} \right)$$

Normalizing each orbital gives

$$\left| c_p \right|^2 = \frac{2}{3}, \quad c_p = \sqrt{\frac{2}{3}} \tag{A.4.11}$$

Thus,

$$\phi_\sigma^1 = \frac{1}{\sqrt{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_{p_x} + 0.\phi_{p_y}$$

$$\phi_\sigma^2 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y} \tag{A.4.12}$$

$$\phi_\sigma^3 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y}$$

This is known as sp^2 hybridization since we have combined one s atomic orbital, and two p atomic orbitals to create three atomic orbitals that contribute individually to σ bonds. The bond angle is 120º.
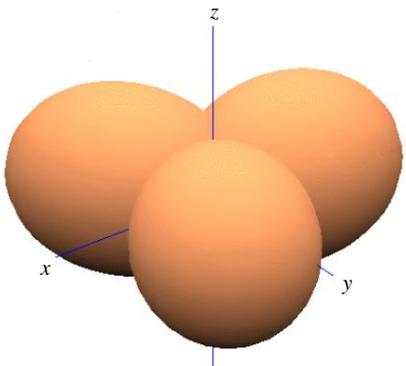

Fig. A 4.6. sp^2 hybridized molecular orbitals point to the vertices of a triangle.

Appendix 4. Hybrid Orbitals

The remaining p_z atomic orbitals will contribute to the frontier molecular orbitals of an sp^2 hybridized material; see for example ethene in Fig. A 4.7.
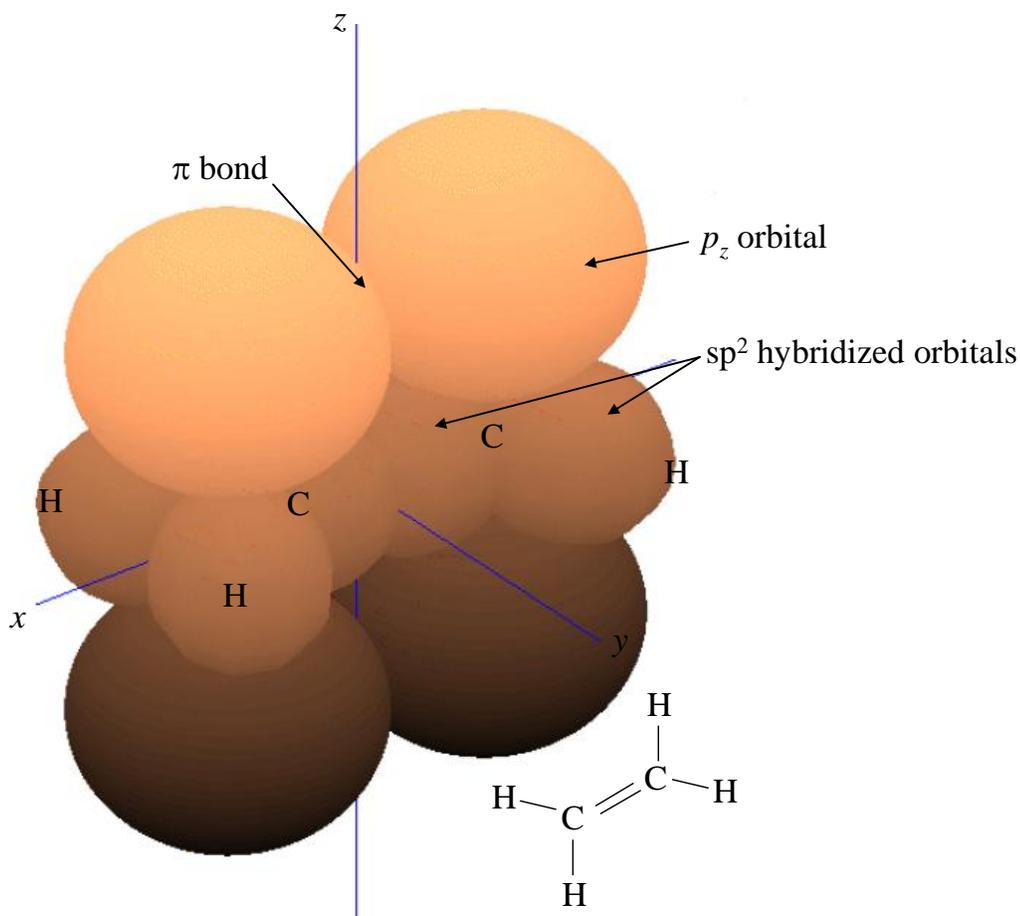

Fig. A 4.7. Ethene contains two sp^2 hybridized carbon atoms. The unhybridized p_z orbitals of carbon form π bonds.

As in the sp hybridized case, electrons in these π molecular orbitals may be delocalized. If electrons are delocalized over several neighboring atoms, then the molecule is said to be *conjugated*. Another sp^2 hybridized material was shown in Fig. 6.2. This is 1,3-butadiene, a chain of $4 \times sp^2$ hybridized carbon atoms. Note the extensive electron delocalization in the π bonds.

Some archetypal conjugated carbon-based molecules are shown in Fig. A 4.8. In each material the carbon atoms are sp^2 hybridized (surrounded by three neighbors at points of an equilateral triangle). Note that another typical characteristic of sp^2 hybridized materials is alternating single and double bonds.
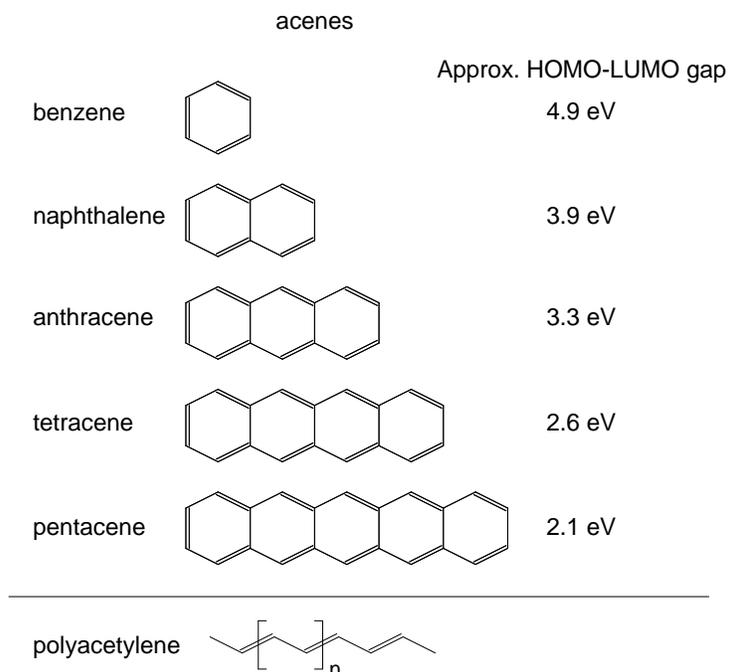
acenes

Approx. HOMO-LUMO gap

benzene   4.9 eV

naphthalene   3.9 eV

anthracene   3.3 eV

tetracene   2.6 eV

pentacene   2.1 eV

polyacetylene

Fig. A 4.8. Examples of conjugated materials frequently employed in electronic devices. Note that the spacing between the HOMO and LUMO energy levels of electrons decrease as the molecules get bigger, consistent with particle in a box predictions of energy level spacing. Adapted from 'Electronic Processes in Organic Crystals' by Pope and Swenberg, First Edition, Oxford University Press, 1982.

Tetrahedral alignment with four neighbors (sp^3 hybridization)

Consider a central atom with four equispaced neighbors. Repulsion between these atoms will push them to the points of a tetrahedron; see Fig. A 4.9.
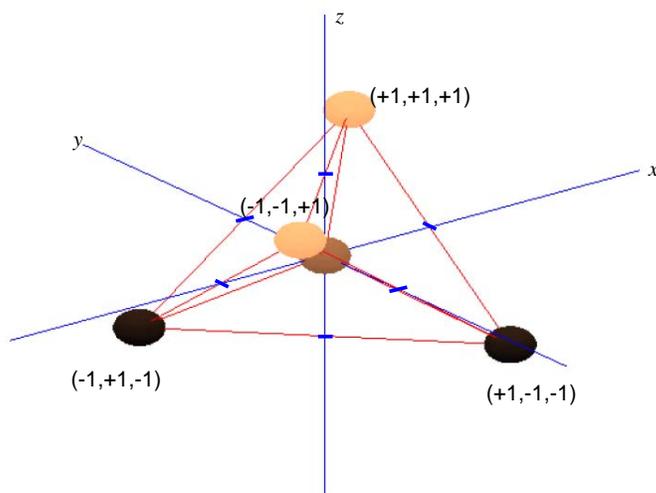
z

(+1,+1,+1)

y

x

(-1,-1,+1)

Fig. A 4.9. Electro-static repulsion forces four atoms surround-ing a central atom to the points of a tetrahedron.

(-1,+1,-1)

(+1,-1,-1)

Now, all atomic orbitals will contribute to σ bonds. There are no π bonds.

Appendix 4. Hybrid Orbitals

Let's define the symmetry adapted atomic orbitals that contribute individually to σ bonds generally as:

$$\phi_\sigma = c_s \phi_s + c_{p_x} \phi_{p_x} + c_{p_y} \phi_{p_y} + c_{p_z} \phi_{p_z} \qquad \text{(A.4.13)}$$

Once again, the *s* orbital contributes equally to all four symmetry adapted atomic orbitals. *i.e.*

$$\left|c_s\right|^2 = \frac{1}{4}, \quad c_s = \frac{1}{2} \qquad \text{(A.4.14)}$$

Since the p_x orbital is aligned with the *x*-axis, p_y with the *y*-axis and p_z with the *z*-axis, we can weight the *p* orbital components by the coordinates of the triangle of neighboring atoms

$$\phi_\sigma^1 = c_s \phi_s + c_p \left(+1\phi_{p_x} + 1\phi_{p_y} + 1\phi_{p_z} \right)$$

$$\phi_\sigma^2 = c_s \phi_s + c_p \left(-1\phi_{p_x} + 1\phi_{p_y} - 1\phi_{p_z} \right)$$

$$\phi_\sigma^3 = c_s \phi_s + c_p \left(+1\phi_{p_x} - 1\phi_{p_y} - 1\phi_{p_z} \right) \qquad \text{(A.4.15)}$$

$$\phi_\sigma^4 = c_s \phi_s + c_p \left(-1\phi_{p_x} - 1\phi_{p_y} + 1\phi_{p_z} \right)$$

Normalizing each orbital gives

$$\left|c_p\right|^2 = \frac{1}{4}, \quad c_p = \frac{1}{2} \qquad \text{(A.4.16)}$$

Thus,

$$\phi_\sigma^1 = \tfrac{1}{2}\left(\phi_s + \phi_{p_x} + \phi_{p_y} + \phi_{p_z} \right)$$

$$\phi_\sigma^2 = \tfrac{1}{2}\left(\phi_s - \phi_{p_x} + \phi_{p_y} - \phi_{p_z} \right)$$

$$\phi_\sigma^3 = \tfrac{1}{2}\left(\phi_s + \phi_{p_x} - \phi_{p_y} - \phi_{p_z} \right) \qquad \text{(A.4.17)}$$

$$\phi_\sigma^4 = \tfrac{1}{2}\left(\phi_s - \phi_{p_x} - \phi_{p_y} + \phi_{p_z} \right)$$

This is known as sp^3 hybridization since we have combined one *s* atomic orbital, and three *p* atomic orbitals to create four possible atomic orbitals that contribute individually to σ bonds. The bond angle is 109.5°.
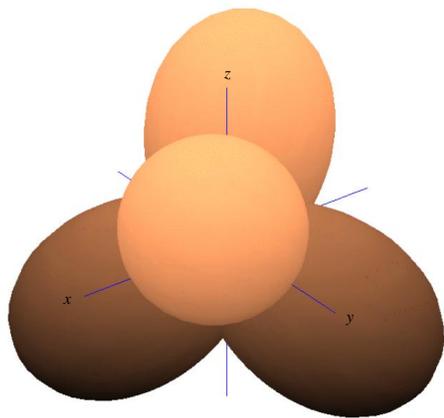

Fig. A 4.10. sp^3 hybridized orbitals point to the vertices of a tetraheron.

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