

**CHM 6480 - Quantum Mechanics  
Handout 3**

**1. Harmonic oscillator – Dirac operator method**

A clever and powerful method for solving the harmonic oscillator was developed by Dirac. The method makes use of operator relationships to find solutions to the harmonic oscillator. The method can also be applied to other problems in quantum mechanics such as rotation in three dimensions.

We begin by defining the position and momentum operators  $\gamma$  and  $\rho$  (operators are bolded,  $\alpha$  is defined below).

$$\gamma = \alpha^{1/2} \mathbf{x} = \alpha^{1/2} x \quad (3.1.1)$$

$$\rho = \frac{\mathbf{p}_x}{\alpha^{1/2} \hbar} \quad (3.1.2)$$

Since

$$\mathbf{p}_x = -i\hbar \frac{d}{dx} = -i\hbar \frac{d}{d\gamma} \frac{d\gamma}{dx} = -i\alpha^{1/2} \hbar \frac{d}{d\gamma} \quad (3.1.3)$$

it follows that

$$\rho = -i \frac{d}{d\gamma} \quad (3.1.4)$$

and therefore

$$\rho^2 = - \frac{d^2}{d\gamma^2} \quad (3.1.5)$$

The Schrodinger equation for the harmonic oscillator can be rewritten in terms of  $\rho$  and  $\gamma$  to get

$$(\rho^2 + \gamma^2) \psi(\gamma) = \varepsilon \psi(\gamma) \quad (3.1.6)$$

where  $\varepsilon = \lambda/\alpha$        $\lambda = 2mE/\hbar^2$        $\alpha = 2\pi m v/\hbar$        $v = (1/2\pi)(k/m)^{1/2}$       (3.1.7)

Now consider the commutator  $[\rho, \gamma] = \rho\gamma - \gamma\rho$ . If we allow  $[\rho, \gamma]$  to operate on some arbitrary function  $f$ , and substitute for the operators for  $\rho$  and  $\gamma$ , we may show that

$$[\rho, \gamma] = -i \quad (3.1.8)$$

It follows from this that

$$(\gamma + i\rho)(\gamma - i\rho) = \gamma^2 + i\rho\gamma - i\gamma\rho + \rho^2 = \gamma^2 + \rho^2 + i[\rho, \gamma] = \gamma^2 + \rho^2 + 1 \quad (3.1.9)$$

$$(\gamma - i\rho)(\gamma + i\rho) = \gamma^2 - i\rho\gamma + i\gamma\rho + \rho^2 = \gamma^2 + \rho^2 - i[\rho, \gamma] = \gamma^2 + \rho^2 - 1 \quad (3.1.10)$$

Note that 3.1.9 and 3.1.10 give different results because  $\gamma$  and  $\rho$  are noncommuting operators. The term in brackets on the left side of eq 3.1.6 can therefore be rewritten as

$$(\rho^2 + \gamma^2) = \frac{1}{2} [ (\gamma^2 + \rho^2 + 1) + (\gamma^2 + \rho^2 - 1) ] = \frac{1}{2} [ (\gamma + i\rho)(\gamma - i\rho) + (\gamma - i\rho)(\gamma + i\rho) ] \quad (3.1.11)$$

If we define two new operators  $\mathbf{a}$  and  $\mathbf{a}^+$  as

$$\mathbf{a} = (1/2)^{1/2} (\boldsymbol{\gamma} + i\boldsymbol{\rho}) \quad (3.1.12)$$

$$\mathbf{a}^+ = (1/2)^{1/2} (\boldsymbol{\gamma} - i\boldsymbol{\rho}) \quad (3.1.13)$$

then it follows that

$$\boldsymbol{\rho}^2 + \boldsymbol{\gamma}^2 = (\mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}) \quad (3.1.14)$$

and our Schrodinger equation (3.1.6) becomes

$$(\mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}) \psi(\boldsymbol{\gamma}) = \varepsilon \psi(\boldsymbol{\gamma}) \quad (3.1.15)$$

Now consider the commutator of  $\mathbf{a}$  and  $\mathbf{a}^+$ . Using Eq 3.1.9, 3.1.10, 3.1.12, and 3.1.13 one can easily show that

$$[\mathbf{a}, \mathbf{a}^+] = \mathbf{a}\mathbf{a}^+ - \mathbf{a}^+\mathbf{a} = 1 \quad (3.1.16)$$

or

$$\mathbf{a}^+\mathbf{a} = \mathbf{a}\mathbf{a}^+ - 1 \quad (3.1.17)$$

$$\mathbf{a}\mathbf{a}^+ = \mathbf{a}^+\mathbf{a} + 1 \quad (3.1.18)$$

By substituting eq 3.1.17 or 3.1.18 into our Schrodinger equation (3.1.15) we may write it in the following two equivalent forms

$$\mathbf{a}\mathbf{a}^+ \psi(\boldsymbol{\gamma}) = [ (\varepsilon/2) + 1/2 ] \psi(\boldsymbol{\gamma}) \quad (3.1.19)$$

$$\mathbf{a}^+\mathbf{a} \psi(\boldsymbol{\gamma}) = [ (\varepsilon/2) - 1/2 ] \psi(\boldsymbol{\gamma}) \quad (3.1.20)$$

We can now do something clever. Consider operating on the left side of both terms of Eq 3.1.19 with  $\mathbf{a}^+$ . This gives

$$\mathbf{a}^+\mathbf{a}\mathbf{a}^+ \psi(\boldsymbol{\gamma}) = [ (\varepsilon/2) + 1/2 ] \mathbf{a}^+\psi(\boldsymbol{\gamma}) \quad (3.1.21)$$

or

$$\mathbf{a}^+\mathbf{a} [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] = [ (\varepsilon/2) + 1/2 ] [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] \quad (3.1.22)$$

But  $[\mathbf{a}^+ \psi(\boldsymbol{\gamma})]$  is just a function, and eq 3.1.22 is just an eigenvalue equation. We have in fact shown is that  $[\mathbf{a}^+ \psi(\boldsymbol{\gamma})]$  is an eigenfunction of the operator  $\mathbf{a}^+\mathbf{a}$  with corresponding eigenvalue  $[ (\varepsilon/2) + 1/2 ]$ . If we now use eq 3.1.17 to substitute for  $\mathbf{a}^+\mathbf{a}$ , we get

$$(\mathbf{a}\mathbf{a}^+ - 1) [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] = [ (\varepsilon/2) + 1/2 ] [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] \quad (3.1.23)$$

or

$$\mathbf{a}\mathbf{a}^+ [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] = [ (\varepsilon/2) + 3/2 ] [\mathbf{a}^+ \psi(\boldsymbol{\gamma})] \quad (3.1.24)$$

So  $[\mathbf{a}^+ \psi(\boldsymbol{\gamma})]$  is also an eigenfunction of  $\mathbf{a}\mathbf{a}^+$ , with corresponding eigenvalue  $[ (\varepsilon/2) + 3/2 ]$ .

Now, if we combine Eq 3.1.22 and 3.1.24, we get

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{a}^+\psi(\gamma)] = [(\epsilon/2) + 1/2 + (\epsilon/2) + 3/2] [\mathbf{a}^+\psi(\gamma)] \quad (3.1.25)$$

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{a}^+\psi(\gamma)] = (\epsilon + 2) [\mathbf{a}^+\psi(\gamma)] \quad (3.1.26)$$

What does this mean? Eq 3.1.26 tells us that if  $\psi(\gamma)$  is an eigenfunction of our Hamiltonian operator  $\mathbf{H} = (\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a})$ , with corresponding eigenvalue  $\epsilon$ , then  $[\mathbf{a}^+\psi(\gamma)]$  is also an eigenfunction of  $\mathbf{H}$ , with eigenvalue  $(\epsilon + 2)$ . Note that while  $[\mathbf{a}^+\psi(\gamma)]$  is an eigenfunction of  $\mathbf{H}$  it is not a normalized eigenfunction. We will discuss this point below. The effect that  $\mathbf{a}^+$  has on a particular eigenfunction is to generate a new eigenfunction of  $\mathbf{H}$ , a state whose energy is higher than that of the original eigenfunction. We therefore call  $\mathbf{a}^+$  a raising operator.

We can repeat this procedure as often as we wish. For example

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{a}^+\mathbf{a}^+\psi(\gamma)] = (\epsilon + 4) [\mathbf{a}^+\mathbf{a}^+\psi(\gamma)] \quad (3.1.27)$$

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+\psi(\gamma)] = (\epsilon + 6) [\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+\psi(\gamma)] \quad (3.1.28)$$

$$\begin{aligned} & \vdots \\ & \vdots \\ & \vdots \\ (\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [(\mathbf{a}^+)^n \psi(\gamma)] &= (\epsilon + 2n) [(\mathbf{a}^+)^n \psi(\gamma)] \end{aligned} \quad (3.1.29)$$

By successive uses of the raising operator  $\mathbf{a}^+$  we can generate the complete set of eigenfunctions corresponding to states of higher energy than  $\psi(\gamma)$ .

Using the same procedure as above, we can also show the following

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{a} \psi(\gamma)] = (\epsilon - 2) [\mathbf{a} \psi(\gamma)] \quad (3.1.30)$$

If  $\psi(\gamma)$  is an eigenfunction of  $\mathbf{H} = (\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a})$ , with corresponding eigenvalue  $\epsilon$ , then  $[\mathbf{a} \psi(\gamma)]$  is also an eigenfunction of  $\mathbf{H}$ , but with eigenvalue  $(\epsilon - 2)$ . The effect that  $\mathbf{a}$  has on a particular eigenfunction of our Schrodinger equation is to generate a new eigenfunction of  $\mathbf{H}$ , a state whose energy is lower than that of the original eigenfunction. We therefore call  $\mathbf{a}$  a lowering operator.

As is the case with  $\mathbf{a}^+$ , we can operate on an eigenfunction  $\psi(\gamma)$  with  $\mathbf{a}$  multiple times, to get

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{aa} \psi(\gamma)] = (\epsilon - 4) [\mathbf{aa} \psi(\gamma)] \quad (3.1.31)$$

$$(\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [\mathbf{aaa} \psi(\gamma)] = (\epsilon - 6) [\mathbf{aaa} \psi(\gamma)] \quad (3.1.32)$$

$$\begin{aligned} & \vdots \\ & \vdots \\ & \vdots \\ (\mathbf{aa}^+ + \mathbf{a}^+\mathbf{a}) [(\mathbf{a})^n \psi(\gamma)] &= (\epsilon - 2n) [(\mathbf{a})^n \psi(\gamma)] \end{aligned} \quad (3.1.33)$$

However, since there is a lowest energy state to the harmonic oscillator, there is a limit as to the number of times we can operate on a particular eigenfunction  $\psi(\gamma)$  with  $\mathbf{a}$ . In fact, if we call the lowest energy (ground) state of the harmonic oscillator  $\psi_0(\gamma)$  we can show that

$$\mathbf{a} \psi_0(\gamma) = 0 \quad (3.1.34)$$

from which it follows that  $\psi_0(\gamma)$  must be the ground state wavefunction.

To use the above method requires method that we know at least one of the eigenfunctions of the harmonic oscillator. Once one of the eigenfunctions has been found, the rest of the eigenfunctions may be generated by successive applications of the raising or lowering operators  $\mathbf{a}^+$  or  $\mathbf{a}$ .

The easiest eigenfunction to find is  $\psi_0(\gamma)$ , the eigenfunction corresponding to the ground state of the harmonic oscillator. If we substitute for  $\mathbf{a}$  in eq 3.1.34, we can obtain the following differential equation for  $\psi_0(\gamma)$

$$\{ (d/d\gamma) + \gamma \} \psi_0(\gamma) = 0 \quad (3.1.35)$$

with solution

$$\psi_0(\gamma) = N_0 \exp(-\gamma^2/2) \quad (3.1.36)$$

where  $N_0$  is a normalization constant. Starting with  $\psi_0(q)$  the complete set of wavefunctions for the harmonic oscillator may be generated

$$\psi_1(\gamma) = (N_1/N_0) [\mathbf{a}^+ \psi_0(\gamma)] \quad (3.1.37)$$

$$\psi_2(\gamma) = (N_2/N_1) [\mathbf{a}^+ \psi_1(\gamma)] = (N_2/N_0) \mathbf{a}^+ \mathbf{a}^+ \psi_0(\gamma) \quad (3.1.38)$$

$$\psi_3(\gamma) = (N_3/N_2) \mathbf{a}^+ \psi_2(\gamma) = (N_3/N_0) \mathbf{a}^+ \mathbf{a}^+ \mathbf{a}^+ \psi_0(\gamma) \quad (3.1.39)$$

$$\begin{array}{l} \vdots \\ \vdots \\ \vdots \\ \vdots \\ \psi_n(\gamma) = (C_n/C_{n-1}) \mathbf{a}^+ \psi_{n-1}(\gamma) = (C_n/C_0) (\mathbf{a}^+)^n \psi_0(\gamma) \end{array} \quad (3.1.40)$$

where  $N_0, N_1, N_2, N_3, \dots N_n \dots$  are normalization constants.

## 2. Expectation values in the operator formalism

Expectation values for solutions to the harmonic oscillator may be found using the same methods used to find expectation values for other systems.

$$\langle O \rangle = \int_{-\infty}^{\infty} \psi_n^* \mathbf{O} \psi_n dx \quad (3.2.1)$$

We can find expectation values by substitution of the appropriate wavefunction and operator and carrying out the integration.

The operator method gives us an easier way to find expectation values for operators that can be written as combinations of the operators of  $\mathbf{p}$  and  $\mathbf{\gamma}$ . Starting from Eq 3.1.12 and 3.1.13 we can show

$$\mathbf{p} = i/(2)^{1/2} (\mathbf{a}^+ - \mathbf{a}) \quad (3.2.2)$$

$$\mathbf{\gamma} = 1/(2)^{1/2} (\mathbf{a}^+ + \mathbf{a}) \quad (3.2.3)$$

Eq 3.1.1 and 3.1.2 may be rewritten to give

$$\mathbf{x} = \mathbf{\gamma}/\alpha^{1/2} \quad (3.2.4)$$

$$\mathbf{p} = \alpha^{1/2} \hbar \mathbf{p} \quad (3.2.5)$$

Using the normalization conditions in eq 3.1.37 – 3.1.40, one may also show, after considerably more work, that

$$\mathbf{a}^+ \psi_n = (n + 1)^{1/2} \psi_{n+1} \quad (3.1.6)$$

$$\mathbf{a} \psi_n = (n)^{1/2} \psi_{n-1} \quad (3.1.7)$$

where  $\psi_n$ ,  $\psi_{n+1}$ , and  $\psi_{n-1}$  are normalized wavefunctions.

The operator formalism and the general properties of solutions to Schrodinger equations now make it possible to evaluate integrals without doing any actual integration. For example,

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^* x \psi_n dx = (1/\alpha)^{1/2} \int_{-\infty}^{\infty} \psi_n^* \gamma \psi_n d\gamma \quad (3.2.8)$$

$$= (1/2\alpha)^{1/2} \int_{-\infty}^{\infty} \psi_n^* (\mathbf{a}^+ + \mathbf{a}) \psi_n d\gamma \quad (3.2.9)$$

$$= (1/2\alpha)^{1/2} \int_{-\infty}^{\infty} \psi_n^* [(n+1)^{1/2} \psi_{n+1} + (n)^{1/2} \psi_{n-1}] d\gamma = 0 \quad (3.2.10)$$

The integrals are equal to zero because the wavefunctions that are solutions to the harmonic oscillator form a complete orthonormal set of functions. Similarly, one can show that

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n dx = (n + 1/2)/\alpha \quad (3.2.11)$$

$$\langle p \rangle = 0 \quad (3.2.12)$$

$$\langle p^2 \rangle = (n + 1/2)\alpha\hbar^2 \quad (3.2.13)$$

The above are particularly easy to derive in Dirac notation. For example, in Dirac notation

$$\begin{aligned} \langle x^2 \rangle &= (1/2\alpha) \langle n | (\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}^+\mathbf{a} + \mathbf{a}\mathbf{a}^+ + \mathbf{a}\mathbf{a}) | n \rangle \\ &= (1/2\alpha) [ 0 + n + (n + 1) + 0 ] = (n + 1/2)/\alpha \end{aligned} \quad (3.2.14)$$

### 3. The Morse potential

The harmonic oscillator potential matches the potential for a real diatomic molecule only in a narrow region around  $r_e$ , the equilibrium bond distance. The Morse potential provides a more realistic model for the potential of a diatomic molecule. There are several ways in which the potential may be written, including the following

$$V(x) = D_e \{ 1 - \exp(- ax) \}^2 \quad (3.3.1)$$

where, as before,  $x = r - r_e$ .  $V(x)$  and  $D_e$ , the dissociation energy, are given in units of wavenumbers ( $\text{cm}^{-1}$ ). The constant  $a$  in eq 3.3.1 is given by the expression

$$a = \{ (2\pi^2 c \mu \omega_e^2) / h D_e \}^{1/2} \quad (3.3.2)$$

where  $\mu$  is the reduced mass of the molecule ( $\mu_{AB} = m_A m_B / (m_A + m_B)$ ) and  $\omega_e = (1/2\pi c) (k/\mu)^{1/2}$  is the vibrational constant, in units of  $\text{cm}^{-1}$ . Note that the value for  $a$  is related to the curvature of the potential at the minimum in the potential energy. A figure showing the Morse potential and comparing it to the harmonic oscillator potential is given below.

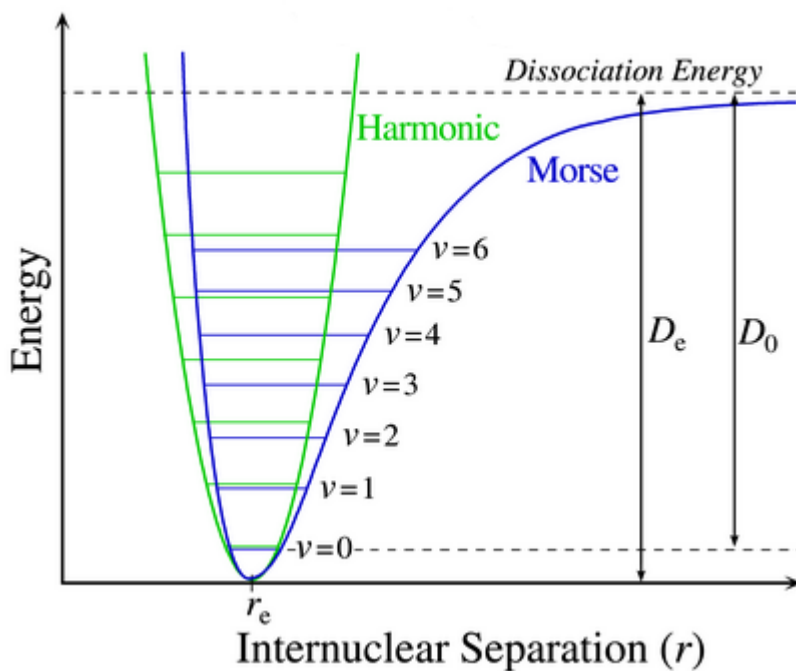


Figure 3.3.1. The Morse potential. Note that we have defined the potential in such a way that the minimum in the potential corresponds to  $V = 0$ .

The Schrodinger equation for the Morse potential can be solved exactly, though the solution is more difficult to find than that for the harmonic oscillator. Somewhat surprisingly, the expression for the energy eigenvalues for a Morse potential takes on a simple form

$$E_n = \omega_e (n + 1/2) - \omega_e x_e (n + 1/2)^2 \quad n = 0, 1, 2, \dots, n_{\max} \quad (3.3.3)$$

where  $E_n$  is in  $\text{cm}^{-1}$  and  $\omega_e x_e = \omega_e^2 / 4D_e$  (note that  $\omega_e x_e$ , despite its appearance, is a single constant). Note that these are simply the first two terms in a power series expansion for  $E_n$  (in terms of powers of  $n + 1/2$ ). Unlike the harmonic oscillator, there are only a finite number of bound states for the Morse potential. As shown in the figure, the states in the Morse oscillator become closer together in energy as  $n$  increases, unlike the harmonic oscillator, which has states equally spaced in energy. Also note that the difference in energy between the  $n^{\text{th}}$  state of a Morse oscillator and the corresponding state of a harmonic oscillator increases with increasing  $n$ .