

# Coulomb Potential Radial Wavefunctions

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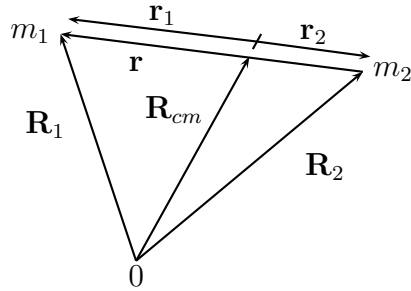
## 1 Reduced Mass Coordinates

In classical mechanics (and quantum) problems involving several particles, it is convenient to separate the motion of the center of mass from the relative motion of the particles. This allows the separation of the motion of the group of particles as a whole (the center of mass motion) from internal motions that can involve mutual potential energies between the particles. These contributions separate out when the energy of the system is computed, as is shown below for two particles.

In the figure below, we start with an origin at 0 and masses at  $\mathbf{R}_1$  and  $\mathbf{R}_2$ . The vector  $\mathbf{r} = \mathbf{R}_1 - \mathbf{R}_2$  is the separation between the two masses and we assume that the interaction potential energy is a function,  $V(\mathbf{r})$ , of this variable. If  $\mathbf{R}_{cm}$  is the center of mass as computed below, then  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of the masses relative to  $\mathbf{R}_{cm}$ . Clearly,

$$\mathbf{R}_1 = \mathbf{R}_{cm} + \mathbf{r}_1 \quad (1)$$

$$\mathbf{R}_2 = \mathbf{R}_{cm} + \mathbf{r}_2 \quad (2)$$



The center of mass is defined as

$$\mathbf{R}_{cm} = \frac{m_1 \mathbf{R}_1 + m_2 \mathbf{R}_2}{m_1 + m_2}. \quad (3)$$

The positions of individual particles *relative to the center of mass* can be obtained as follows (using just two particles):

$$\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_{cm} = \mathbf{R}_1 - \frac{m_1 \mathbf{R}_1 + m_2 \mathbf{R}_2}{m_1 + m_2} \quad (4)$$

$$= \frac{m_1 \mathbf{R}_1 + m_2 \mathbf{R}_1 - m_1 \mathbf{R}_1 - m_2 \mathbf{R}_2}{m_1 + m_2} \quad (5)$$

$$= \frac{m_2 (\mathbf{R}_1 - \mathbf{R}_2)}{m_1 + m_2} = \frac{m_2}{m_1 + m_2} \mathbf{r}. \quad (6)$$

Similarly,

$$\mathbf{r}_2 = -\frac{m_1}{m_1 + m_2} \mathbf{r} \quad (7)$$

Check that these make sense in the limit where one of the masses is much greater than the other.

The energy is

$$E = \frac{1}{2} m_1 \dot{\mathbf{R}}_1^2 + \frac{1}{2} m_2 \dot{\mathbf{R}}_2^2 + V(\mathbf{r}) \quad (8)$$

but,

$$\frac{1}{2} m_1 \dot{\mathbf{R}}_1^2 = \frac{1}{2} m_1 \left( \dot{\mathbf{R}}_{cm} + \frac{m_2}{m_1 + m_2} \dot{\mathbf{r}} \right)^2 \quad (9)$$

$$= \frac{1}{2} m_1 \dot{\mathbf{R}}_{cm}^2 + \frac{1}{2} \frac{m_1 m_2^2}{(m_1 + m_2)^2} \dot{\mathbf{r}}^2 + \frac{m_1 m_2}{m_1 + m_2} \dot{\mathbf{R}}_{cm} \cdot \dot{\mathbf{r}} \quad (10)$$

and

$$\frac{1}{2} m_2 \dot{\mathbf{R}}_2^2 = \frac{1}{2} m_2 \dot{\mathbf{R}}_{cm}^2 + \frac{1}{2} \frac{m_1^2 m_2}{(m_1 + m_2)^2} \dot{\mathbf{r}}^2 - \frac{m_1 m_2}{m_1 + m_2} \dot{\mathbf{R}}_{cm} \cdot \dot{\mathbf{r}}. \quad (11)$$

[Check the units!] In the energy, the last terms above sum to zero:

$$E = \frac{1}{2} M \dot{\mathbf{R}}_{cm}^2 + \frac{1}{2} \mu \dot{\mathbf{r}}^2 + V(\mathbf{r}) \quad (12)$$

with the total mass,

$$M = m_1 + m_2 \quad (13)$$

and the reduced mass,  $\mu$ , given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (14)$$

[What happens to this calculation when there are multiple particles,  $m_i$  at  $\mathbf{R}_i$ ? Ans: The dot product terms should again sum to zero.]

Center-of-mass coordinates take the origin to be located at  $\mathbf{R}_{cm}$ , so in these coordinates,  $E = \frac{1}{2} \mu \dot{\mathbf{r}}^2 + V(\mathbf{r})$  which involves only the relative coordinates of the particles. The momentum associated with the relative coordinate is  $\mathbf{p} = \mu \dot{\mathbf{r}}$ , so we can also write  $E = \frac{1}{2\mu} \mathbf{p}^2 + V(\mathbf{r})$ . Some examples follow:

1. *The  $N_2$  molecule: two equal masses.* Here,

$$\mathbf{R}_{cm} = \frac{1}{2} (\mathbf{R}_1 + \mathbf{R}_2), \quad \mathbf{r}_1 = -\mathbf{r}_2 \quad (15)$$

and

$$\mu = \frac{1}{2} m_N, \quad (16)$$

where  $m_N$  is the mass of a single nitrogen atom. The center of mass is half way between the particles. The potential energy describes the binding potential associated with the chemical bond as a function of the bond length,  $|\mathbf{r}| = r$ .  $V(r)$  is attractive at large  $r$ ,

has a minimum at some  $r_0$ , and becomes repulsive at smaller  $r$ . The energy relative to the center of mass is

$$E = \frac{1}{2\mu}\mathbf{p}^2 + V(r) = \frac{1}{m_N}\mathbf{p}^2 + V(r). \quad (17)$$

In the absence of external forces (or potentials), the center of mass will move with constant momentum while the atoms rotate and vibrate about the center of mass. In a gravitational potential, the same force acts on both objects, effectively acting on the center of mass, so the center of mass follows the usual parabolic path while the atoms rotate and vibrate as before.

2. *The Earth-Sun system: very different masses.* Here,

$$\mathbf{R}_{cm} = \frac{m_E\mathbf{R}_E + m_S\mathbf{R}_S}{m_E + m_S} \quad (18)$$

$$= \frac{\mathbf{R}_S + \frac{m_E}{m_S}\mathbf{R}_E}{1 + m_E/m_S}. \quad (19)$$

The ratio of masses is  $m_E/m_S = 6 \times 10^{24}\text{kg}/2 \times 10^{30}\text{kg} = 3 \times 10^{-6}$ , so

$$\mathbf{R}_{cm} = \mathbf{R}_S + 3 \times 10^{-6}\mathbf{R}_E. \quad (20)$$

If we take  $\mathbf{R}_S = 0$  as our origin, then  $\mathbf{R}_{cm} = (3 \times 10^{-6})(1.5 \times 10^{11})\text{m} = 4.5 \times 10^5\text{m} = 450\text{km}$ . But the sun's radius is  $7 \times 10^8\text{m}$ , so  $R_{cm}/R_{sun} \sim 10^{-3}$ . We find that the center of mass of the earth-sun system is only one one-thousandth of the sun's radius from the center of the sun! The relative coordinate is  $\mathbf{r} = \mathbf{R}_E - \mathbf{R}_S \approx \mathbf{R}_E - \mathbf{R}_{cm}$  and we can think of the earth rotating around the center of the sun.

3. *An interacting electron and proton.* Since  $m_e = m_p/1836$ ,  $\mu = 1836m_e^2/1837m_e = 0.9995m_e$ . This is less unbalanced than the earth-sun system, we still tend to think of the electron orbiting the heavy proton. However, with precision optical measurements, one can easily see this correction to a calculation using  $m_e$ . We therefore use the reduced mass here.

The quantum mechanical Hamiltonian can now be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r, \theta, \phi). \quad (21)$$

For a spherically symmetric interaction potential, everything we have done with angular momentum carries through. We simply replace the mass,  $m$ , of a single particle with the reduced mass,  $\mu$ , for the pair.

## 2 The Radial Equation for the Coulomb potential

For angular momentum eigenstates, we can write

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r). \quad (22)$$

The time independent Schrodinger equation becomes, with separation of variables in the form  $\psi(r, \theta, \phi) = R(r)Y_l^{m_l}(\theta, \phi)$ ,

$$\hat{H}R(r) = ER(r) \quad (23)$$

since the angle dependent functions  $Y_l^{m_l}(\theta, \phi)$  commute with  $\hat{H}$  and can be canceled. Writing this out yields,

$$-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} [rR(r)] + \frac{\hbar^2 l(l+1)}{2\mu r^2} R(r) + V(r)R(r) = ER(r). \quad (24)$$

Multiplying through by  $r$  and defining  $u(r) = rR(r)$  gives

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} u(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} u(r) + V(r)u(r) = Eu(r) \quad (25)$$

or

$$u''(r) - l(l+1) \frac{u(r)}{r^2} - \frac{2\mu}{\hbar^2} V(r)u(r) = -\frac{2\mu}{\hbar^2} Eu(r) \quad (26)$$

Now, for the hydrogen atom, we have the Coulomb potential,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (27)$$

so  $\frac{2\mu}{\hbar^2} V(r) = -\frac{2}{a_0 r}$ , with  $a_0 = \hbar^2 4\pi\epsilon_0 / \mu e^2 = 0.529\text{\AA}$ , the radius of the first Bohr orbit. We also write

$$k^2 = \frac{2\mu(-E)}{\hbar^2}, \quad (28)$$

but note that, while  $k$  is not literally a wavevector, it has the appropriate units and it has the familiar dependence on the energy. Since we are interested in describing bound states, the eigenvalues,  $E$ , will be less than zero and  $k$  will be real. We can write our differential equation as

$$u'' - l(l+1) \frac{u}{r^2} + \frac{2}{a_0} \frac{u}{r} = k^2 u. \quad (29)$$

For large  $r$ , the middle terms become small and this reduces to

$$u'' = k^2 u \quad (30)$$

and we get

$$u(r) \propto e^{-kr} \quad (31)$$

We expect the wavefunctions to decay exponentially to zero at large  $r$  where  $V(r) > E$ .

As we did for the harmonic oscillator, we now introduce a new function,

$$u(r) = v(r)e^{-kr} \quad (32)$$

and we substitute this into (29) to obtain

$$v''(r) - l(l+1)\frac{v(r)}{r^2} - 2kv'(r) + \frac{2}{a_0}\frac{v}{r} = 0. \quad (33)$$

Terms involving  $k^2$  have conveniently canceled. Keep in mind that the energy is buried in the parameter  $k$ .

At this point, we again resort to a brute force power series expansion for  $v(r)$ . The lowest power in the series has to be  $r$  to at least the first power since our radial wavefunction is  $R(r) = u(r)/r = [v(r)/r]e^{-kr}$  and this must be finite as  $r \rightarrow 0$ . Just as with the harmonic oscillator, we will also have to check that the power series leads to the limit  $R(r) \rightarrow 0$  as  $r \rightarrow \infty$ ; this will again require a finite number of terms and will lead to energy quantization. We have the following:

$$v(r) = \sum_{p=1}^{\infty} A_p r^p \quad (34)$$

$$v'(r) = \sum_1 p A_p r^{p-1} \quad (35)$$

$$v''(r) = \sum_2 p(p-1) A_p r^{p-2} = \sum_1 p(p+1) A_{p+1} r^{p-1} \quad (36)$$

$$\frac{v(r)}{r} = \sum_1 A_p r^{p-1} \quad (37)$$

$$\frac{v(r)}{r^2} = \sum_1 A_p r^{p-2} = A_1 r^{-1} + \sum_2 A_p r^{p-2} = A_1 r^{-1} + \sum_1 A_{p+1} r^{p-1}. \quad (38)$$

In the last equation, the first term in the sum has been separated out so that the remaining terms can be written in the same way (same summation limits, same powers of  $r$ ) as the previous expressions. On substitution, we have a sum of powers of  $r$ ; in order for this sum to be zero for general  $r$ , the coefficients of each power must be zero and this leads to

$$[p(p+1) - l(l+1)] A_{p+1} = 2 \left[ kp - \frac{1}{a_0} \right] A_p \quad (39)$$

$$\text{and } l(l+1) A_1 = 0. \quad (40)$$

As in the harmonic oscillator case, we again obtain a recursion relation giving coefficients in the power series expansion. This time, however, the recursion relation gives coefficients of successive powers instead of skipping a power.

**Zero angular momentum.** For the case  $l = 0$  (where  $Y_0^0(\theta, \phi) = \text{constant}$ ),  $A_1$  is allowed to be non-zero and the recursion relation (39) gives us the following coefficients in the power series for  $v(r)$ . We need to check whether  $u(r) = v(r)/e^{kr}$  is well-behaved at large  $r$  where

the high powers of  $r$  will dominate. We need to compare the coefficients in  $v(r)$  to those in the expansion of the exponential. For large  $p$  we have from (39)

$$p^2 A_{p+1} = 2kpA_p \quad (41)$$

or

$$\frac{A_{p+1}}{A_p} = \frac{2k}{p}, \quad (42)$$

whereas the exponential is

$$e^{kr} = \sum_{p=0}^{\infty} \frac{1}{p!} (kr)^p \quad (43)$$

with ratios of coefficients of successive terms being  $k/p$ . Thus,  $v(r)$  will diverge unless we terminate the series at some  $p_{max} = n$  by making  $kn = 1/a_0$  (see Eq. 39) or

$$k_n = \frac{1}{na_0}. \quad (44)$$

$n$  can be any integer from 1 to  $\infty$ . Plugging all the constants back in, this yields a condition on the energy:

$$E_n = -\frac{\hbar^2 k_n^2}{2\mu} = -\frac{\hbar^2}{2\mu a_0^2} \frac{1}{n^2} = -\frac{\mu e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2} = -[13.6\text{eV}] \frac{1}{n^2}. \quad (45)$$

This is precisely the Bohr formula for the energy levels.

We can now re-write the recursion relation with this quantization condition (we keep  $l$  since the same series termination condition has to apply when  $l \neq 0$ ):

$$[p(p+1) - l(l+1)] A_{p+1} = \frac{2}{a_0} \left[ \frac{p}{n} - 1 \right] A_p \quad (46)$$

$$\text{and } l(l+1) A_1 = 0. \quad (47)$$

Let's look at some special cases:

$l = 0, n = 1$ . We can set  $A_1 = 1$  and we get  $A_{p>1} = 0$  by substituting  $p = 1$  and  $n = 1$  into (46) and noticing that the square bracketed quantity on the left will always be non-zero. This yields (see Eq. 34), using the notation,  $R_{n,l}(r)$  for the radial function,

$$R_{1,0}(r) = \frac{v(r)}{r} e^{-k_1 r} = e^{-r/a_0}. \quad (48)$$

This wavefunction is finite at  $r = 0$  and decays exponentially with increasing  $r$  with a decay length equal to the first Bohr orbit radius or  $0.528\text{\AA}$ . Furthermore,

$$\psi(r, \theta, \phi) = N e^{-r/a_0}, \quad (49)$$

where  $N$  is a normalization constant, since  $Y_0^0 = \text{constant}$ .

$l = 0, n = 2$ . Again, we set  $A_1 = 1$ . The recursion relation (46) with  $p = 1$  and  $n = 2$ , gives  $A_2 = \frac{1}{2} \frac{2}{a_0} (-\frac{1}{2}) A_1 = -\frac{1}{2a_0}$ . Plugging in  $p = n = 2$  gives zero for  $A_3$  and all successive coefficients so that

$$R_{2,0}(r) = \frac{r - 0.5r^2/a_0}{r} e^{-k_2 r} = \left(1 - \frac{1}{2} \frac{r}{a_0}\right) e^{-r/2a_0} \quad (50)$$

Again the wavefunction is isotropic (i.e., independent of the angle variables), is finite at the origin, and decays exponentially – but now with a decay constant of twice the Bohr radius. The probability function extends farther from the origin than in the  $n = 1$  case and this corresponds to the reduced binding energy compared to the ground state.

*Finite angular momentum.* When  $l > 0$ , we have to require that  $A_1 = 0$  (because of Eq. 47) which at first appears to force all coefficients to be zero. However, when we reach  $p = l$ , where  $l = 1, 2, 3, \dots$ , the coefficient multiplying  $A_{p+1}$  (or  $A_{l+1}$ ) is zero and the recursion is satisfied for non-zero  $A_{l+1}$ . The final catch is to notice that, in order for the series to terminate, we have to require that  $n > l$  since otherwise, the term in square brackets on the right side of (46) is already greater than zero and will continue to be for increased  $p$ . Hence, these states have the identical quantization condition (identical energy eigenvalues) to those with  $l = 0$ .

$l = 1$ .  $A_1 = 0$  but, since the square bracket on the left side of (46) is zero for  $p = 1$ ,  $A_2$  can be non-zero. However, when we plug in  $p \geq 2$ , the left side coefficient is positive and the right side contains the factor  $p/n - 1$ ; if  $n = 1$ , this is always positive and the expansion will contain arbitrarily large powers of  $r$ . If  $n > 1$ , the series terminates when we reach  $p = n$ .

For example, if  $l = 1$  and  $n = 2$ , the series contains only one term,  $A_2$ , so

$$R_{2,1}(r) = \frac{r}{a_0} e^{-r/2a_0}, \quad (51)$$

where the  $1/a_0$  is inserted in the pre-factor to keep the dimensions as they are in  $R_{n0}(r)$  expressions above. The generalization is that the wavefunctions with  $l > 0$  go to zero at the origin and have the same exponential decay as the  $l = 0$  functions at large  $r$ . As  $n$  increases at fixed  $l$ , more terms appear in the polynomial pre-factor. Note also that the radial functions have no dependence on  $m_l$ , the azimuthal quantum number and the energy has no dependence on either  $l$  or  $m_l$ . The lack of dependence of the energy on  $l$  is unique to the  $1/r$  form for the potential energy.

See the text, page 139 for a list of wavefunctions with radial and angular variations included as well as proper normalization.

The above results for quantum number possibilities are best summarized by grouping first by the principle quantum number,  $n$ , and then listing the allowed values for the angular momentum: these are called “orbitals” and can be specified as  $|n, l, m_l \rangle$  as in

$ 1, 0, 0 \rangle$	$E_1 = -13.6 \text{ eV}$	$L^2 = 0$	$L_z = 0$
$ 2, 0, 0 \rangle$	$E_2 = -3.4 \text{ eV}$	$L^2 = 0$	$L_z = 0$
$ 2, 1, -1 \rangle$	$E_2 = -3.4 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = -\hbar$
$ 2, 1, 0 \rangle$	$E_2 = -3.4 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = 0$
$ 2, 1, 1 \rangle$	$E_2 = -3.4 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = \hbar$
$ 3, 0, 0 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 0$	$L_z = 0$
$ 3, 1, -1 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = -\hbar$
$ 3, 1, 0 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = 0$
$ 3, 1, 1 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 2\hbar^2$	$L_z = \hbar$
$ 3, 2, -2 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 6\hbar^2$	$L_z = -2\hbar$
$ 3, 2, -1 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 6\hbar^2$	$L_z = -\hbar$
$ 3, 2, 0 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 6\hbar^2$	$L_z = 0$
$ 3, 2, 1 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 6\hbar^2$	$L_z = \hbar$
$ 3, 2, 2 \rangle$	$E_3 = -1.51 \text{ eV}$	$L^2 = 6\hbar^2$	$L_z = 2\hbar$

At each principle quantum number there are

$$g(n) = \sum_{l=0}^{n-1} (2l + 1) = n^2 \quad (52)$$

degenerate orbitals. When we add the electron’s spin, we would specify  $|n, l, m_l, m_s \rangle$  or, better yet,  $|n, l, j, m_j \rangle$ ; in either case we have  $2n^2$  quantum states.<sup>1</sup> For one electron atoms, if  $l = 0$ ,  $j = \frac{1}{2}$ , whereas for  $l > 0$ ,  $j = l \pm \frac{1}{2}$ . All one electron atomic (or ionic) states possess angular momentum and an associated magnetic moment.

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<sup>1</sup>Okay, this isn’t really complete either since the proton has spin,  $s = 1/2$  – here we have to add all three angular momentum contributions to get a new  $j$  quantum number and associated  $m_j$  and there would be  $4n^2$  states. The scale for nuclear magnetic moments is  $\mu_n = \frac{e\hbar}{2m_p} \sim \mu_B/1836$  so the interaction energies (the *hyperfine interaction*) are quite small. For most purposes, there is little distinction (very little energy difference, very little change in wavefunctions) between the states with differently oriented proton spin – chemically speaking, these two states can be neglected and we say there are  $2n^2$  states at each  $n$  or energy level.