Central potentials and the hydrogen atom

Now I would like to discuss a very important problem in 3D quantum mechanics; namely, two particles connected by a potential that depends only on the distance:

The interaction potential depends only on the separation the particles

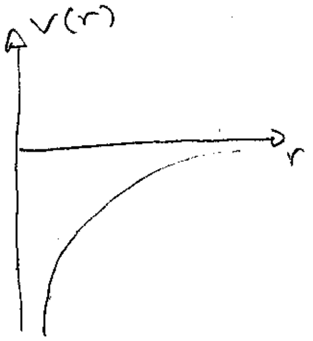
$$V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|) \tag{1}$$

his is what we call a central potential

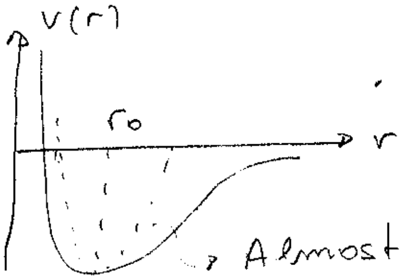
The total Hamiltonian is therefore

$$\hat{H} = \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|) \tag{2}$$

Example 1: the hydrogen atom $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$



Example 2: diatomic molecule $\quad V(r) \approx \frac{1}{2} k (r-r_0)^2$



→ Almost a parabola.

It is possible to sepparate Eq (2) into 2 commuting terms. Define

$$\boxed{\vec{R} = \frac{m_1 \vec{r_1} + m_2 \vec{r_2}}{m_1 + m_2}} = \text{position of the center of ma} \qquad (3)$$

and

$$\boxed{\vec{r} = \vec{r_1} - \vec{r_2}} = \text{relative position} \qquad (4$$

I leave to you as an exercise to find the inverses

$$\vec{r_1} = \vec{R} + \frac{m_2}{M} \vec{r} \qquad (5)$$

$$\vec{r_2} = \vec{R} - \frac{m_1}{M} \vec{r}$$

where $\quad M = m_1 + m_2 = \text{total mass} \qquad (6)$

The momentum of the center of mass is the total momentum. Since momentum is an additive quantity it reads

$$\underline{\vec{P}} = \vec{p}_1 + \vec{p}_2 \tag{7}$$

We also define the relative momentum

$$\vec{p} = \frac{m_2 \vec{p}_1 - m_1 \vec{p}_2}{m_1 + m_2} \tag{8}$$

I know this definition is weird, but you will see in a moment that it makes sense. The inverses are

$$\begin{aligned} \vec{p}_1 &= \vec{p} + \frac{m_1}{M}\underline{\vec{P}} \\ \vec{p}_2 &= -\vec{p} + \frac{m_2}{M}\underline{\vec{P}} \end{aligned} \tag{9}$$

Now we substitute these new variables in the Hamiltonian (2):

$$\hat{H} = \frac{1}{2m_1}\left[\vec{p} + \frac{m_1}{M}\underline{\vec{P}}\right]^2 + \frac{1}{2m_2}\left[-\vec{p} + \frac{m_2}{M}\underline{\vec{P}}\right] + V(r)$$

$$= \frac{1}{2m_1}\left[\vec{p}^{\,2} + \frac{m_1^2}{M^2}\underline{\vec{P}}^2 + \frac{2m_1}{M}\vec{p}\cdot\underline{\vec{P}}\right] +$$

$$+ \frac{1}{2m_2}\left[\vec{p}^{\,2} + \frac{m_2^2}{M^2}\underline{\vec{P}}^2 - \frac{2m_2}{M}\vec{p}\cdot\underline{\vec{P}}\right] + V(r)$$

Note how the cross term cancels!

$$\hat{H} = \frac{1}{2}\left[\frac{m_1 + m_2}{M^2}\right]\vec{P}^2 + \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\vec{p}^2 + V(\vec{r})$$

In the first term $(m_1 + m_2)/M^2 = 1/M$. In the 2nd term we define the reduced mass

$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \text{or} \qquad m = \frac{m_1 m_2}{m_1 + m_2} \qquad (10)$$

Then we obtain

$$\boxed{\hat{H} = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2m} + V(r)} \qquad (11)$$

Note how the Hamiltonian is factored in 2 terms. The first term describes the free motion of the center of mass and the 2nd term corresponds to the relative motion of the two particles.

We may therefore diagonalize these two terms sepparat Recall that when we have two non-interacting systems, the energies are sums and the wave functions are products

There is a catch, however. what I just said will only be true if the 2 parts of $\hat{H}$ commute. Moreover, it must be true that $\vec{r}$ and $\vec{p}$ obey the canonical commutation relations. I leave all this for you as an exercise.

the motion of the center of mass is just like that of a free particle. Hence, we don't need to worry about it anymore.

Thus our problem is reduced to a study of the Hamiltonian

$$\hat{H} = \frac{\vec{p}^{\,2}}{2m} + V(r) + -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad (12)$$

In spherical coordinates we have seen that

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{r^2} \qquad (13)$$

here L^2 is the angular momentum operator defined n units of $\hbar$

$$L^2 = -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} \qquad (14)$$

Since we are dealing with a central potential, pherical coordinates are useful. Hence we want our wave functions in terms of r, θ and ϕ. Our goal is then to solve

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{r^2}\right\}\psi + V(r)\psi = E\psi \qquad (15)$$

The entire angular part is contained in L^2. We already know the eigenvalues and eigenfunctions of this part. They are

$$L^2 Y_\ell^m = \ell(\ell+1) Y_\ell^m \qquad (16)$$

Hence let us try for our solution of (15) the product

$$\psi(r,\theta,\phi) = R(r)\, Y_\ell^m(\theta,\phi) \qquad (17)$$

Inserting this in (15) we find

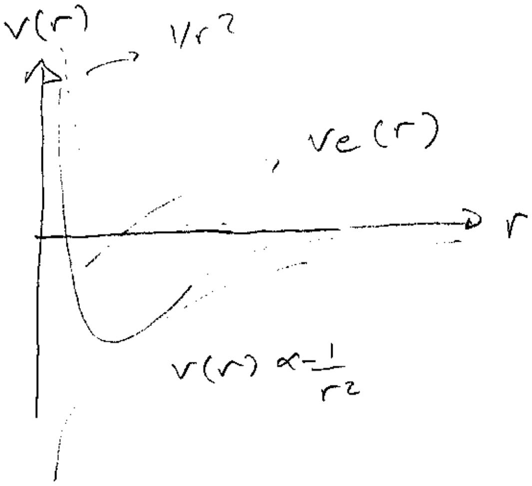
$$\boxed{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2}{2m}\ell(\ell+1) + V(r)\right]R = ER} \qquad \text{(1}$$

This is called the radial equation. It is an Eq for $R(r)$ only. This is what is nice about central potentials: the wave function always factors as a product of a radial part and an angular part. Moreover, the eigenfunctions of the angular part are the spherical Harmonics, so that part is alrea completely solved.

Note also how the angular momentum appears in the radial equation in the form of an effective potential

$$V_e(r) = V(r) + \frac{\hbar^2}{2m}\,\frac{\ell(\ell+1)}{r^2} \qquad (19)$$

this new term acts like a centrifugal force which ends to keep the particle away from the nucleus.



Another thing I need to talk about is normalization. In spherical coordinates we must have

$$\int |\psi|^2\, r^2 \sin\theta \, d\theta \, d\phi \, dr = 1 \qquad (20)$$

the spherical Harmonics in (17) are already normalized

$$\int |Y_\ell^m|^2 \sin\theta \, d\theta \, d\phi = 1 \qquad (21)$$

Hence, the normalization of the radial part becomes

$$\int_0^\infty |R(r)|^2 r^2 dr = 1 \qquad (22)$$

therefore we interpret

$$\boxed{|R(r)|^2 r^2 = \text{radial probability distribution}} \qquad (23)$$

With this in mind it is also convenient to define

$$R(r) = \frac{u(r)}{r} \qquad (24)$$

then
$$\frac{dR}{dr} = \frac{u'}{r} - \frac{u}{r^2}$$

$$r^2\frac{dR}{dr} = ru' - u$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = u' + ru'' - u' = ru''$$

Thus Eq (18) becomes

$$-\frac{\hbar^2}{2m}\frac{ru''}{r^2} + \left[\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} + V(r)\right]\frac{u}{r} = E\frac{u}{r}$$

Hence the new radial Eq becomes

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} + V(r)\right]u = Eu} \qquad (25)$$

This is exactly like the 1D Schrödinger Eq for a potential

$$\tilde{V}(r) = \begin{cases} \infty & r < 0 \\ V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} & r > 0 \end{cases} \qquad (26)$$

The function $u(r)$ is normalized as

$$\int_0^\infty |u(r)|^2 \, dr = 1 \qquad (27)$$

To proceed further we must specify $V(r)$

Random, out of place, comment

We have therefore learned that the angular part of the wavefunction corresponds to the spherical harmonics. If we look only at the angular part we have

$$\psi(r,\theta,\phi) \propto e^{im\phi}$$

This function must be periodic in ϕ:

$$\psi(r,\theta,\phi+2\pi) = \psi(r,\theta,\phi)$$

because if we rotate our system by 360° we get back where we started. Thus we must have

$$e^{im2\pi} = 1$$

This will only be true for m integer. This is yet another reason why l cannot be a $1/2$ integer.

The Hydrogen atom

We now reach the problem which started it all: the hydrogen atom. When Schrödinger first proposed his equation he immediately applied it to the Hydrogen atom and verified that he could reproduce experimental results such as the Balmer series. Hence, this is <u>the</u> most important problem in QM.

For the H-atom the potential is

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad (28)$$

We will also include an extra ingredient and write Ze^2 instead of e^2. This way we can also account for the case of ionized He, doubly ionized Lithium, etc.

It is also convenient to define

$$q^2 = \frac{Ze^2}{4\pi\varepsilon_0} \qquad (29)$$

so that

$$V(r) = -\frac{q^2}{r} \qquad (30)$$

[this is the same as using CGS units].

Eq (25) now becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{q^2}{r}\right]u = E\,u \qquad (31)$$

We are interested in bound states so $E < 0$. Thus we define

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \quad \text{or} \quad E = -\frac{\hbar^2\kappa^2}{2m} \qquad (32$$

then,

$$\frac{d^2u}{dr^2} + \left[-\frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}\frac{q^2}{r}\right]u = \kappa^2 u \qquad (33)$$

Now we need to define a dimensionless position. The convenient choice is

$$\rho = \kappa r \qquad (34)$$

Dividing (33) by κ^2 we get

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} + \left[-\frac{l(l+1)}{\kappa^2 r^2} + \frac{2m}{\hbar^2}\frac{q^2}{\kappa^2 r}\right]w = u$$

We now see that it is also convenient to define

$$\rho_0 = \frac{2m}{\hbar^2}\frac{q^2}{\kappa} \qquad (35)$$

We then finally obtain

$$\boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u} \qquad (36)$$

This is a good example of a beautiful Eq: everything is dimensionless and it only has two parameters: ρ_0 and ℓ.

The next step is to trim down the assumptotic parts of this Eq. First we look at $\rho \to \infty$. Then $1/\rho$ and $1/\rho^2$ are all negligible so that

$$\frac{d^2u}{d\rho^2} \approx u \qquad (\rho \to \infty) \qquad (37)$$

This has two solutions

$$u(\rho) = A e^{-\rho} + B e^{\rho} \qquad (38)$$

But e^{ρ} diverges and we can't have that so we choose only $e^{-\rho}$.

Next we look at $\rho \to 0$. In this case the most important term is $1/\rho^2$ so that

$$\frac{d^2u}{d\rho^2} \approx \frac{\ell(\ell+1)}{\rho^2} u \qquad (\rho \to 0) \qquad (39)$$

The general solution is

$$u(\rho) = C\rho^{l+1} + \frac{D}{\rho^{l}} \qquad (40)$$

(please check this). Again, $1/\rho^{l}$ blows up as $\rho \to 0$ so the only solution we want is ρ^{l+1}.

We now know how $u(\rho)$ will behave when $\rho \to \infty$ and $\rho \to 0$. We therefore cut down these dependencies by defining

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \qquad (41)$$

We substitute this in (36).

Now comes the ugly part: we need to have faith!

$$u' = (l+1)\rho^{l} e^{-\rho} v - \rho^{l+1} e^{-\rho} v + \rho^{l+1} e^{-\rho} v'$$

$$= \rho^{l} e^{-\rho}\left[(l+1-\rho)v + \rho v'\right]$$

$$u'' = \left(l\rho^{l-1} e^{-\rho} - \rho^{l} e^{-\rho}\right)\left[\dots\right] + $$

$$+ \rho^{l} e^{-\rho}\left[-v + (l+1-\rho)v' + v' + \rho v''\right]$$

$$= \rho^{l} e^{-\rho}\left\{\left[\frac{l}{\rho} - 1\right]\left[(l+1-\rho)v + \rho v'\right] + \right.$$

$$\left. + \left[-v + (l+2-\rho)v' + \rho v''\right]\right\}$$

$$u'' = \rho^{\ell} e^{-\rho}\Big\{(\ell-\rho)v' + \frac{\ell(\ell+1)}{\rho}v - \ell v - (\ell+1-\rho)v$$
$$- v + (\ell+2-\rho)v' + \rho v''\Big\}$$

$$= \rho^{\ell} e^{-\rho}\Big\{\Big[\frac{\ell(\ell+1)}{\rho} - 2\ell - 2 + \rho\Big]v + 2(\ell+1-\rho)v' + \rho v''\Big\}$$

I know things don't look good, but have some patience. Now we insert this in (36):

$$\Big[\frac{\ell(\ell+1)}{\rho} - 2\ell - 2 + \rho\Big]v + 2(\ell+1-\rho)v' + \rho v'' = \rho v - \rho_0 v + \frac{\ell(\ell+1)}{\rho}v$$

We therefore obtain

$$\boxed{\rho v'' + 2(\ell+1-\rho)v' + [\rho_0 - 2(\ell+1)]v = 0} \qquad (42)$$

otice how, by doing this transformation, we eliminated all poles of the equation.

Now what we do is try to express v as a power series:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \qquad (43)$$

he game now is to write the derivatives in terms of owers of ρ^j.

then

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j\, c_j \rho^{j-1} = \sum_{j=1}^{\infty} j\, c_j \rho^{j-1}$$

$\uparrow$ since $j=0$ gives zero anyway

Now make $k = j-1$. then

$$\frac{dv}{d\rho} = \sum_{k=0}^{\infty} (k+1)\, c_{k+1}\, \rho^{k}$$

Since k is a dummy index we may go back to j:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} (j+1)\, c_{j+1}\, \rho^{j} \qquad (44)$$

Similarly

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j\,(j+1)\, c_{j+1}\, \rho^{j-1}$$

$$\rho\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j\,(j+1)\, c_{j+1}\, \rho^{j} \qquad (45)$$

For the term $\rho v'$ we write instead

$$\rho\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j\, c_j \rho^{j}$$

Inserting every thing back in (42) we conclude that

$$\sum_{j=0}^{\infty} \left\{ j(j+1)\, c_{j+1} + 2(\ell+1)(j+1)\, c_{j+1} - 2j\, c_j + \right.$$
$$\left. + \left[\rho_0 - 2(\ell+1)\right] c_j \right\} \rho^j = 0$$

For the solution to be valid for any ρ, each term must be zero. Hence we conclude that

$$\left[(j+1)(j+2\ell+2)\right] c_{j+1} + \left[2j + \rho_0 - 2\ell - 2\right] c_j = 0$$

or

$$\boxed{c_{j+1} = \frac{\left[2(j+\ell+1) - \rho_0\right]}{(j+1)(j+2\ell+2)}\, c_j} \qquad (46)$$

this is a <u>recursion</u> <u>relation</u>. It determines the constant c_{j+1} given that you know c_j. Thus we start with c_0, which is an arbitrary constant, and then determine $c_1, c_2, \ldots$

Now comes an important question: is this series infinite? We answer this by analyzing the recursion formula when j is large. Then we get

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

[I don't drop the +1 just for convenience]. Suppose for now that this is exact. Then

$$c_j \approx \frac{2^j}{j!} c_0$$

so that

$$v(\rho) \approx c_0 \sum_{j=0} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

Hence

$$u(\rho) \approx \rho^{l+1} e^{-\rho} e^{2\rho} = \rho^{l+1} e^{\rho}$$

This blows up as $\rho \to \infty$. This is precisely the solution we discarded before.

We therefore conclude that the series must terminate, that is, there must exist a value j_{max} such that

$$2(j_{max} + l + 1) = \rho_0 \qquad (47)$$

Let us define

$$n = j_{max} + l + 1 \tag{48}$$

then

$$\rho_0 = 2n$$

Recalling our definition of ρ_0 in Eq (35) we see that

$$\frac{2m}{\hbar^2}\,\frac{q^2}{\kappa} = 2n$$

$$\kappa = \frac{q^2 m}{\hbar^2}\,\frac{1}{n}$$

or

$$\kappa^2 = -\frac{2mE}{\hbar^2} = \frac{q^4 m^2}{\hbar^4}\,\frac{1}{n^2}$$

Thus

$$\boxed{E_n = -\frac{m q^4}{2\hbar^2}\,\frac{1}{n^2} = \frac{E_1}{n^2}} \tag{49}$$

These are the energies of the Hydrogen atom. Note how quantization of energy follows from us imposing that the series must terminate. But this, in turn, is the condition for the existence of bound states. Since j_{max} and l are both integers

$$\boxed{n = 1, 2, 3, \ldots} \tag{50}$$

We can also write everything in SI units

$$\boxed{E_1 = -\frac{m}{2\hbar^2} z^2 \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx -13.6\ \text{eV}} \qquad (51)$$

We also define

$$\boxed{a = \frac{\hbar^2}{mq^2} = \text{Bohr radius}} \qquad (52)$$

then

$$\kappa = \frac{1}{an} \qquad (53)$$

and

$$\rho = \frac{r}{an} \qquad (54)$$

The recurrence Eq (46) is, in terms of n

$$\boxed{c_{j+1} = \frac{2(j+l+1-n)\,c_j}{(j+1)(j+2l+2)}} \qquad (55)$$

these coefficients determine $v(\rho)$ from which we obtain the radial part of the wave function as

$$R(r) = \frac{u}{r} = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho)$$

or

$$\boxed{R_{nl}(r) = \frac{1}{r}\left(\frac{r}{an}\right)^{l+1} e^{-r/an}\, v\left(\frac{r}{an}\right)} \qquad (56)$$

Ground State : $n = 1$

The energy is

$$E_1 = -13.6\ eV \qquad (57)$$

and corresponds to the ionization energy of hydrogen. Let us apply Eq (42), the maximum value of j is given by (48):

$$j_{max} = n - l - 1 = -l$$

But j cannot be negative. Thus we must have

$$l = 0 \qquad (58)$$

The value of n restricts the allowed values of l. The only non-zero coefficient is therefore c_0 so that

$$R(r) = \frac{1}{r}\left(\frac{r}{a \times 1}\right)^{0+1} e^{-r/a \times 1}\ c_0$$

or

$$R_{10}(r) = \frac{c_0}{a}\ e^{-r/a} \qquad (59)$$

he value of c_0 is determined from normalization. Since $l = 0 \rightarrow m = 0$ the ground state wave function is

$$\boxed{\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}}\ e^{-r/a}} \qquad (60)$$

here I already include the correct normalization.

$n=2$

when $n=2$ the energy is

$$E_2 = \frac{E_1}{4} = -3.4\,eV$$

Eq (48) now implies

$$j_{max} = 2 - l - 1 = 1 - l$$

Hence we may have $l=0$ or $l=1$ (both have the same energy). If $l=0$ Eq (55) gives

$$c_{j+1} = \frac{2(j+0+1-2)}{(j+1)(j+2)}\,c_j = \frac{2(j-1)}{(j+1)(j+2)}\,c_j$$

thus

$$c_1 = -c_0$$

$$c_2 = 0$$

therefore

$$R_{20}(r) = \frac{1}{r}\left(\frac{r}{2a}\right)^{0+1} e^{-r/2a}\left[c_0 - c_0\left(\frac{r}{2a}\right)\right]$$

$$R_{20}(r) = \frac{c_0}{2a}\left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

For each set of n and l, the c_j are completely different.

In general, for arbitrary n, l can take on the values

$$\boxed{l = 0, 1, 2, \ldots, n-1} \qquad (61)$$

Since for each l there are $2l+1$ values of m, the degeneracy of the n-th level is

$$\boxed{d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2} \qquad (62)$$

The polynomials $v(\rho)$ are called Associated Laguerre Polynomials. Apart from normalization

$$v(\rho) = \mathcal{L}_{n-l-1}^{2l+1}(2\rho) \qquad (63)$$

If we include the normalization we may finally write

$$\boxed{R_{nl}(r) = \frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{(n+l)!}}\left(\frac{2r}{n}\right)^{l} e^{-r/na}\,\mathcal{L}_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)} \qquad (64)$$

so the complete wavefunctions of the hydrogen atom are

$$\boxed{\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi)} \qquad (65)$$

these wavefunctions form a basis for the space of functions of spherical coordinates:

$$\boxed{\int \psi^{*}_{n\ell m}\,\psi_{n'\ell'm'}\,dV = \delta_{nn'}\,\delta_{\ell\ell'}\,\delta_{mm'}} \qquad (66)$$