Bound States

Since a lot of material on bound states is covered in undergraduate quantum mechanics, we will only cover some unusual situations here.

Hydrogen atom in Parabolic Coordinates

Usually this problem is solved in spherical coordinates. However, for some perturbation problems (motion in a uniaxial field) it is more convenient to have the wavefunctions expressed in parabolic coordinates.

We start with a two-particle Hamiltonian

$$\hat{H} = \frac{\vec{P}_e^{\,2}}{2m_e} + \frac{\vec{P}_p^{\,2}}{2m_p} - \frac{e^2}{|\vec{Q}_e - \vec{Q}_p|}$$

We then change variables to the centre-of-mass and relative coordinates

$$\vec{Q}_c = \frac{m_e \vec{Q}_e + m_p \vec{Q}_p}{m_e + m_p} \qquad \vec{Q}_r = \vec{Q}_e - \vec{Q}_p .$$

$$\vec{P}_c = \vec{P}_e + \vec{P}_p \qquad \vec{P}_r = \frac{m_p \vec{P}_e - m_e \vec{P}_p}{m_e + m_p}$$

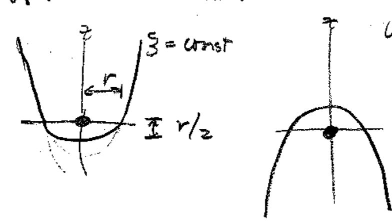
So the Hamiltonian becomes

$$H = \frac{\vec{P}_c^{\,2}}{2M} + \frac{\vec{P}_r^{\,2}}{2\mu} - \frac{e^2}{|\vec{Q}_r|}$$

$r = \frac{\xi}{1-\cos\theta}$

Introduce the coordinates

$$\xi = r - z = r(1-\cos\theta)$$
$$\eta = r + z = r(1+\cos\theta)$$
$$\varphi = \varphi$$



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The operator p^2 becomes, in these coordinates,

$$-\hbar^2 \left[\frac{4}{\xi+\eta} \left\{ \frac{\partial}{\partial\xi}\xi\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta} \right\} + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2} \right].$$

Hence we write the Schrodinger equation as (after factoring out the time dependence as usual):

$$-\frac{\hbar^2}{2\mu}\left[\frac{4}{\xi+\eta} \left\{ \frac{\partial}{\partial\xi}\xi\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta} \right\} + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2} \right]\psi - \frac{2e^2}{\xi+\eta}\psi = E\psi$$

This form looks as if it will separate out just as the S.E. does in spherical polars. Anticipating solving only the bound state problem, we put $E = -|\epsilon|$ and factor $\psi(\xi,\eta,\phi) = f(\xi)g(\eta)\Phi(\phi)$. As usual, we find

$$\Phi(\phi) = e^{im\phi} \qquad \text{(normalization put elsewhere).}$$

Multiply by $\dfrac{-\mu(\xi+\eta)}{2\hbar^2\psi}$ gives

this is quantum #, not μ

$$\frac{1}{f}\frac{d}{d\xi}\xi\frac{df}{d\xi} + \frac{1}{g}\frac{d}{d\eta}\eta\frac{dg}{d\eta} - \frac{m^2(\xi+\eta)}{4\xi\eta} - \frac{\mu|\epsilon|(\xi+\eta)}{2\hbar^2} = -\frac{\mu e^2}{\hbar^2}$$

This equation separates into two equations once we use $\dfrac{\xi+\eta}{\xi\eta} = \dfrac{1}{\eta} + \dfrac{1}{\xi}$:

$$\frac{1}{f}\frac{d}{d\xi}\xi\frac{df}{d\xi} - \left[\frac{m^2}{4\xi} + \frac{\mu|\epsilon|\xi}{2\hbar^2}\right] = -k_1$$

$$\frac{1}{g}\frac{d}{d\eta}\eta\frac{dg}{d\eta} - \left[\frac{m^2}{4\eta} + \frac{\mu|\epsilon|\eta}{2\hbar^2}\right] = -k_2$$

$$k_1 + k_2 = -\frac{\mu e^2}{\hbar^2}.$$

These two equations are identical in form, as one would expect from the form of the coordinate system chosen.

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Solution

Replace z with a dimensionless variable $s = \gamma\xi$,
where $\gamma^2 = \frac{2\mu|E|}{\hbar^2}$.

$$\Rightarrow \frac{1}{s}\frac{d}{ds}s\frac{df}{ds} + \left[\frac{\lambda_1}{s} - \frac{1}{4} - \frac{m^2}{2s^2}\right]f = 0 \qquad \text{with } \lambda_1 = \frac{k_1}{\gamma}.$$

The solution to this equation has the asymptotic form

$$f(s) = e^{\pm s/2} \qquad \text{for } \frac{1}{s}\frac{d}{ds}s\frac{df}{ds} - \frac{1}{4}f \simeq 0$$

Hence, one does the usual substitution

$$f(s) = s^k \, L(s) \, e^{-s/2}$$

Boundary conditions give $k = \frac{1}{2}|m|$

Again, this is angular momentum quantum number, not mass.

These are associated Laguerre polynomials $L(s) = L^{|m|}_{n_1+|m|}(s)$

with $n_1 = \lambda_1 - \frac{1}{2}(|m|+1)$
$= 0, 1, 2, 3 \ldots$

Now, both solutions for λ have the same form

$$\lambda_1 = n_1 + \tfrac{1}{2}(|m|+1) \qquad (n_1, n_2 = 0, 1, 2 \ldots)$$
$$\lambda_2 = n_2 + \tfrac{1}{2}(|m|+1)$$

$$\Rightarrow \lambda_1 + \lambda_2 = n \quad (= n_1 + n_2 + |m| + 1) \qquad n = 1, 2, 3 \ldots$$

But $\lambda_1 + \lambda_2 = \frac{1}{\gamma}(k_1 + k_2) = \left(\frac{\hbar^2}{2\mu|E|}\right)^{1/2}\left(-\frac{\mu e^2}{\hbar^2}\right)$

$$\Rightarrow (\lambda_1 + \lambda_2)^2 = \frac{\hbar^2}{2\mu|E|}\left(\frac{\mu^2 e^4}{\hbar^4}\right) \Rightarrow |E| = \frac{\mu e^4}{2\hbar^2(\lambda_1+\lambda_2)^2} \quad \text{or } E = -\frac{\mu e^4}{2\hbar^2 n^2}.$$

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So, we find that the expression for the energy is the same as that found for spherical polar coordinates.

Estimates from Indeterminacy Relations

Order of magnitude vs Statistical Bounds

One often makes order of magnitude estimates on the basis of the dimensional argument $r \cdot p \sim \hbar$. While this order of magnitude argument often uses the indeterminacy relations for justification, in fact we should link these two relations. There are strict inequalities implied by the indeterminacy relations, but they are not the same as $r \cdot p \sim \hbar$.

For example, lets return to the 1-D expression

$$\Delta_r^2 \ \Delta_p^2 \geq \frac{\hbar^2}{4}.$$

In a 3-D situation, this reads for the components

$$\langle (r_\alpha - \bar{r}_\alpha)^2 \rangle \cdot \langle (P_\beta - \bar{P}_\beta)^2 \rangle \geq \frac{\hbar^2}{4} \delta_{\alpha\beta}.$$

where $\bar{a} = \langle a \rangle$

Suppose now that we specialize to bound states and place our origin such that $\bar{r}_\alpha = 0$. Then

$$\langle r_\alpha^2 \rangle \cdot \langle P_\beta^2 \rangle \geq \frac{\hbar^2}{4} \delta_{\alpha\beta}.$$

Summing over β at fixed α yields $\langle r_\alpha^2 \rangle \langle \vec{P}^2 \rangle \geq \frac{\hbar^2}{4}$

or $\langle \vec{r}^2 \rangle \langle \vec{P}^2 \rangle \geq 3\hbar^2/4$.

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We can take this one step further by assuming spherical symmetry, so that

$$\langle \vec{r}^{\,2} \rangle = 3 \langle r_\alpha^2 \rangle \qquad \langle \vec{P}^{\,2} \rangle = 3 \langle P_\alpha^2 \rangle .$$

$$\Rightarrow \quad \langle \vec{r}^{\,2} \rangle \langle \vec{p}^{\,2} \rangle \geq \frac{9\hbar^2}{4} \qquad \text{(spherical sym).}$$

This relationship is exact, not order of magnitude. If there is no momentum dependent potential present, then $KE = \vec{P}^{\,2}/2\mu$ and

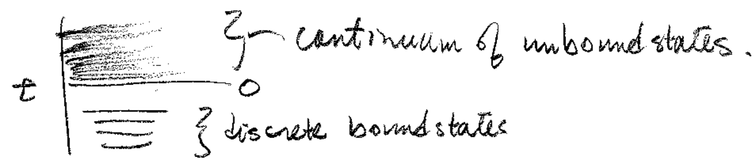
$$\langle \vec{r}^{\,2} \rangle \langle KE \rangle \geq \frac{9\hbar^2}{8\mu} .$$

This states that the smaller a bound state is, the higher its kinetic energy must be.

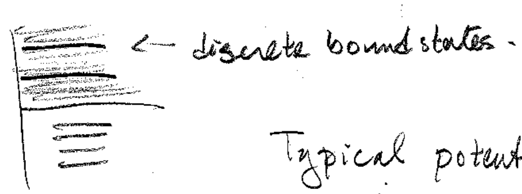
An Unusual Bound State (Ballentine, pg. 205-207).

We complete Chap. 10 [Bound states] with a somewhat counter-intuitive example: There exist some potentials with positive energy bound states.

Usual situation



Possible:



Typical potential for this kind of state to occur is $W(r) = \dfrac{-4k\sin(2kr)}{r}$ $\qquad E_{BS} = +\frac{1}{2}k^2$

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