Nonrelativistic Hydrogen Atom

Refs: Sakurai, App. A.5 & A.6; Davydov, Secs. 34, 38 & 39.

1) About the only nontrivial QM problem in atomic physics that can be solved exactly is that of a (spinless) point electron $(-e, m)$ moving in the Coulomb field of a (spinless) point "proton" $(+Ze, M)$. Here we review that problem, in anticipation of adding some bells & whistles later, via perturbation theory.

The electron-proton interaction potential $V(r) = -Ze^2/r$ ¶ is spherically symmetric, and so we are concerned with solutions to the time-independent Schrödinger Eqtn (in 3D) which respect this symmetry. Spherical polar coordinates (r, θ, φ) are appropriate, and we find straightforwardly...

$$\left\{-(\hbar^2/2\mu)\nabla^2 + V(r)\right\}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad \text{express } \nabla^2 \text{ in } (r,\theta,\varphi) \text{ cds,}^\star$$

$$\text{write: } \psi(\mathbf{r}) = \frac{1}{r}R(r)Y_{\ell m}(\theta,\varphi);$$

$$\Rightarrow \boxed{-\frac{\hbar^2}{2\mu}\frac{d^2R}{dr^2} + \left[V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right]R = ER}; \quad \ell = 0, 1, 2, \ldots \tag{1}$$

REMARKS

1. When force center has mass M and object particle (electron) has mass m, then "reduced mass" $\mu = mM/(m+M)$ enters Eq. (1) [and r = CM cd, etc].

2. ℓ is the ∡ momentum quantum #. It appears as a separation cnst for the ∡ variation, or -- in QM parlance -- because the ∡ momentum operator $\hat{\mathbf{L}}^2 = -\hbar^2\hat{\Lambda}$ appears as a commuting operator on the LHS of Eq. (1).

3. The spherical harmonics $Y_{\ell m}(\theta,\varphi)$ express ψ's ∡ dependence universally for all

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* $\nabla^2 = \frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{\Lambda}\right\}$, w/ $\hat{\Lambda} = \frac{1}{\sin\theta}\left\{\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$.

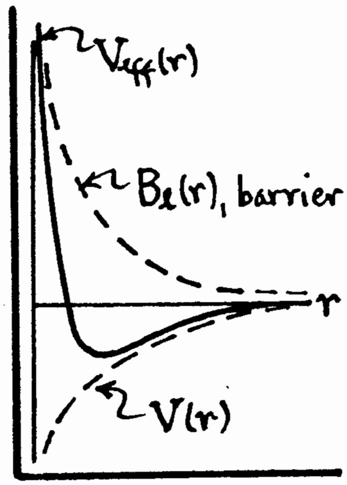
¶ $Z=1 \Rightarrow H^0$-atom, $Z=2 \Rightarrow He^+$-ion, etc. These are single-e "hydrogenlike atoms."

central force potentials $V(r)$. They are eigenfcns of $\hat{\mathbf{L}}^2 = -\hbar^2\hat{\Lambda}$ & $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$:

$$\left[\begin{array}{l} \hat{\mathbf{L}}^2 Y_{lm}(\theta,\varphi) = [l(l+1)\hbar^2]\, Y_{lm}(\theta,\varphi)\ ;\ l = 0,1,2,\ldots\ ; \\ \hat{L}_z Y_{lm}(\theta,\varphi) = [m\hbar]\, Y_{lm}(\theta,\varphi)\ ;\ m = -l, -l+1, \ldots, +l \ \Big\}\ \begin{array}{l}2l+1\\ \text{values}.\end{array} \end{array}\right. \qquad (2)$$

For each value of l, there is a $(2l+1)$-fold degeneracy in the allowed m-values.

<u>4.</u> The term in l in Eq. (1) is effectively a (repulsive) addition to the interaction $V(r)$, omnipresent when $l \neq 0$. In fact we can write Eq. (1) as...



$$\left[\begin{array}{l} \frac{d^2R}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V_{eff}(r)\right] R = 0, \qquad (3) \\ \text{w/}\ V_{eff}(r) = V(r) + B_l(r),\quad B_l(r) = \frac{l(l+1)\hbar^2}{2\mu r^2}\ \Big\}\ \underline{\text{centrifugal barrier}} \end{array}\right.$$

As sketched, an otherwise attractive $V(r)$ will become a repulsive $V_{eff}(r)$ as $r \to 0$.

<u>5.</u> <u>Re Eq. (1), note miscellaneous facts</u>:

<u>a.</u> $\frac{1}{r}R(r)$ must $\to$ finite as $r \to 0$, so $R(r) \propto r^{1+\epsilon}$, $\epsilon \geq 0$, as $r \to 0$.

<u>b.</u> $R(r)$ & energy E will depend on ∡ momentum quantum # l. As well, for bound states (when $R(\infty) = 0$), $R(r)$ & E can depend on new quantum #s.

<u>c.</u> The states ψ have a definite <u>parity</u>. Under the inversion operator $\hat{\mathcal{P}}$...

$$\longrightarrow \hat{\mathcal{P}}(r,\theta,\varphi) = (r, \pi-\theta, \varphi+\pi)\ :\ \hat{\mathcal{P}}\, Y_{lm}(\theta,\varphi) = (-)^l\, Y_{lm}(\theta,\varphi). \qquad (4)$$

So, states ψ with $\left\{\begin{array}{c}\text{even}\\ \text{odd}\end{array}\right\}$ l have $\left\{\begin{array}{c}\text{even}\\ \text{odd}\end{array}\right\}$ inversion symmetry. This classification is allowed because $\hat{\mathcal{P}}$ is a commuting operator: $[\hat{\mathcal{P}}, \hat{\Lambda}] = 0$.

<u>d.</u> In the form of Eq. (3), the radial eqtn is ready for the WKB approxn:

$$\left[\!\left[\frac{d^2R}{dr^2} + k^2(r)\, R = 0, \ \text{w/}\ k(r) = \sqrt{\frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]} \right]\!\right] \Big\}\ \begin{array}{l}\text{WKB form}\\ \text{(more, later)}\end{array} \qquad (5)$$

6. A rough idea of what to expect for bound-state central force problems may be obtained from a rough integration of the radial eqtn, as follows.

$$\int_\infty |\psi|^2 d^3x = \int_0^\infty |R(r)/r|^2 r^2 dr \underbrace{\int_{4\pi} |Y_{\ell m}|^2 d\Omega}_{=1} = 1$$

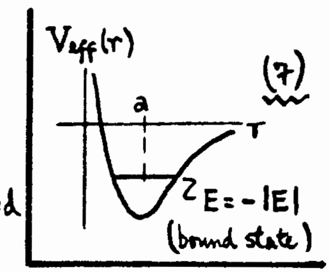
$$\xrightarrow{\text{so}} \int_0^\infty |R(r)|^2 dr = 1, \text{ and: } R(\infty) \to 0, \text{ for bound state problems.} \quad (6)$$

Assume $R(r)$ is real, and integrate $\int_0^\infty R(r)\{\text{Eq.(1)}\}\,dr \ldots$

$$\int_0^\infty dr\, R(r) \times \{\text{Eq.(1)}\} \Rightarrow -\frac{\hbar^2}{2\mu} \underbrace{\int_0^\infty dr\, R \frac{d^2R}{dr^2}}_{= R\left(\frac{dR}{dr}\right)\Big|_0^\infty - \int_0^\infty dr\,(dR/dr)^2} + \int_0^\infty dr\, R^2 \left[V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right] = E$$

$= \cancel{R\left(\frac{dR}{dr}\right)\Big|_0^\infty} \to 0$ $- \int_0^\infty dr\,(dR/dr)^2$, partial integration

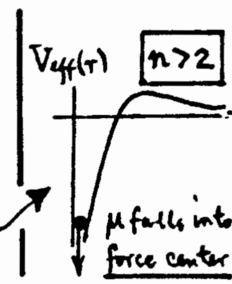
$$\text{so } \left[\!\left[E = \int_0^\infty dr\, R^2 \left\{ \frac{\hbar^2}{2\mu}\left[\frac{1}{R}\left(\frac{dR}{dr}\right)\right]^2 + V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right\}. \right]\!\right] \quad (7)$$



Now suppose $V(r)$ is binding, so that the particle μ is confined to a small region $0 \lesssim r \sim a$. Approx'ly: $\frac{1}{R}\left(\frac{dR}{dr}\right) \sim a$,† and:

$$E \simeq \int_0^\infty dr\, R^2 \left\{ \frac{\hbar^2}{2\mu a^2} + V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right\}\Big|_{r=a} \;;\; \text{put } V(r) = -C/r^n,$$

$$\text{so } \underline{\underline{E \simeq -\frac{C}{a^n} + \frac{\hbar^2}{2\mu a^2}[1 + \ell(\ell+1)] = E(a).}} \quad (8)$$



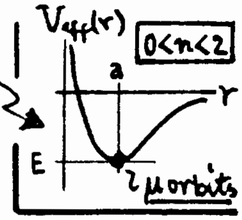
Now locate a by looking for a minimum in E vs. a.

$n > 2$ ⇒ graph at right. Min. E is at $a = 0$; μ falls into force center.

$0 < n < 2$ ⇒ graph at right. ∃ a real min; μ orbits at finite a & E.

$$\frac{\partial E}{\partial a} = 0 \Rightarrow \begin{cases} a^{2-n} = [1 + \ell(\ell+1)]\hbar^2/n\mu C, \\ E = -(2-n)(\hbar^2/2\mu n)[1 + \ell(\ell+1)]. \end{cases} \quad (9)$$

Classically, stable orbits only for $n < 2$.



† As $r \to \infty$, and for $V(r) \to 0$, Eq.(1) goes over to: $R'' + \left(\frac{2\mu E}{\hbar^2}\right)R \simeq 0$. For a boundstate, $E = -|E|$, and the solution $R(r) \sim e^{-r/a}$, $\text{w/ } a = \frac{\hbar^2}{2m|E|}$, automatically shows $|R'| \sim R/a$.

2) Before we do the Coulomb problem $V(r) = -Ze^2/r$ in detail, it is worth remarking that several other QM problems with spherical symmetry can be solved, and prove useful as a starting point for various calculations.

A. Free particle with given l : $V(r) \equiv 0$ [Davydov, ¶ 35]. (10)

$R_l(r) = A_l\,[r j_l(kr)] \leftarrow$ sph. Bessel fcn; $k = \sqrt{(2\mu/\hbar^2)E}$ unlimited.

Useful for QM theory of scattering by central forces.

B. Motion in a 3D rectangular well : $V(r) = \begin{cases} 0, & r \leq a, \\ \infty, & r > a. \end{cases}$ [Davydov, ¶ 36]. (11)

$\psi(\mathbf{r}) \propto j_l(kr) Y_{lm}(\theta, \varphi)$, $0 \leq r \leq a$; $\psi \equiv 0$ @ $r > a$.

$\Rightarrow$ energies : $E_{nl} = \hbar^2 k_n^{(l)2}/2\mu$, w/ $j_l(k_n^{(l)} a) = 0$ $\begin{cases} l = 0, 1, 2, \ldots \\ n = 1, 2, 3, \ldots \end{cases}$

Generalization of standard QM problem in 1D.

C. 3D symmetric oscillator : $V(r) = \frac{1}{2}\mu\omega^2 r^2$ [Davydov, ¶ 37]. (12)

$R_{nl}(r) \propto \xi^{l+1} e^{-\frac{1}{2}\xi^2}\, \Phi(-n, l + \frac{3}{2}, \xi^2)$ $\begin{cases} \xi = r/a,\ a = \sqrt{\hbar/\mu\omega}, \\ \Phi = \text{confluent hypergeometric fcn}; \end{cases}$

w/ $l = 0, 1, 2, \ldots$ (as above), and $n = 0, 1, 2, \ldots$ in order that $R(\xi \to \infty) \to 0$;

energies : $E_{nl} = (2n + l + \frac{3}{2})\hbar\omega$.

Useful for elementary models of nuclear binding.

There are a few others (molecular binding) which we will do by other means.

We shall get back to the free particle problem with spherical symmetry when we study scattering theory.

But now we will do the details of the H-atom problem.

Nowel. H-atom

H|4

FIND FIFTY STATES

S	T	T	E	S	U	H	C	A	S	S	A	M	T	R	S	M	Z	A	O	R	U
N	M	S	A	K	C	I	K	L	P	B	V	R	S	Y	A	V	E	M	A	A	W
A	N	O	Z	I	R	A	I	N	I	G	R	I	V	T	S	E	W	I	D	N	Y
A	I	N	R	O	F	I	L	A	C	U	A	Z	X	Y	S	R	G	N	I	A	K
N	O	T	G	N	I	H	S	A	W	L	N	A	B	S	T	M	E	N	R	I	C
S	O	U	T	H	D	A	K	O	T	A	N	E	E	J	J	O	O	E	O	S	U
M	A	R	Y	L	A	N	D	L	M	I	H	N	W	N	O	N	R	S	L	I	T
O	P	U	T	A	H	R	S	T	L	N	N	U	E	J	V	T	G	O	F	U	N
A	K	A	X	H	O	A	W	O	I	E	Y	Z	A	V	E	R	I	T	S	O	E
K	R	L	S	B	C	D	R	E	T	F	C	I	J	K	A	R	A	A	X	L	K
S	O	A	A	I	N	A	V	L	Y	S	N	N	E	P	M	D	S	N	O	P	E
A	Y	S	X	H	C	S	R	N	A	G	I	H	C	I	M	N	A	E	T	U	R
R	W	K	E	H	O	W	Y	O	M	I	N	G	V	S	A	X	Y	S	Y	A	H
B	E	A	T	C	E	M	F	I	L	G	H	T	I	K	L	I	K	I	E	O	O
E	N	U	K	L	M	N	A	H	M	I	H	E	R	C	A	R	T	N	H	D	D
N	O	R	T	H	D	A	K	O	T	A	N	A	G	L	B	N	I	D	U	A	E
S	R	I	R	U	O	S	S	I	M	I	T	A	I	S	A	A	S	I	N	R	I
N	E	W	H	A	M	P	S	H	I	R	E	B	N	O	M	O	R	A	E	O	S
X	G	I	P	P	I	S	S	I	S	S	I	M	I	V	A	V	W	N	S	L	L
Y	O	C	I	X	E	M	W	E	N	D	E	L	A	W	A	R	E	A	Z	O	A
X	N	I	S	N	O	C	S	I	W	R	T	S	A	N	A	T	N	O	M	C	N
T	T	U	C	I	T	C	E	N	N	O	C	S	I	O	N	I	L	L	I	X	D