

APAS 5110. Internal Processes in Gases. Fall 1999.

Hydrogen Atom without Spin

1. SCHRÖDINGER EQUATION

Schrödinger's equation describes the time evolution of the wavefunction ψ in nonrelativistic quantum mechanics

$$i\hbar \frac{\partial}{\partial t} \psi = H\psi , \quad (1.1)$$

where H is a Hermitian operator called the Hamiltonian. Schrödinger's equation is linear in the wavefunction ψ , so that the sum of any two solutions of the equation is also a solution.

The Hamiltonian operator H of a single particle of mass m is postulated to be the sum of the kinetic energy operator $p^2/2m$ and the potential energy operator V

$$H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m} \nabla^2 + V . \quad (1.2)$$

If the Hamiltonian H is not explicitly dependent on time, then it commutes with the energy operator $i\hbar\partial/\partial t$

$$\left[i\hbar \frac{\partial}{\partial t}, H \right] = 0 . \quad (1.3)$$

According to the general principle, this means that there exist eigenfunctions $\psi(t, \mathbf{x})$ which are simultaneously eigenfunctions of the energy operator $i\hbar\partial/\partial t$ and of the Hamiltonian H , with eigenvalue the energy E

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi = H\psi . \quad (1.4)$$

Equation (1.4) implies that the eigenfunction $\psi(t, \mathbf{x})$ is separable into a factor $e^{-i\omega t}$ which depends on time, and a factor $\phi(\mathbf{x})$ which is independent of time

$$\psi(t, \mathbf{x}) = e^{-i\omega t} \phi(\mathbf{x}) , \quad (1.5)$$

with $E = \hbar\omega$. Physically, the eigenfunction ψ has a definite energy E : its energy is conserved. This is an example of the general principle that a quantity is conserved if and only if the corresponding operator commutes with the Hamiltonian.

The spatial eigenfunction $\phi(\mathbf{x})$ in equation (1.5) satisfies the time-independent Schrödinger equation

$$H\phi = E\phi . \quad (1.6)$$

2. CONSERVATION OF PARTICLE PROBABILITY

The quantity $\psi^\dagger\psi$ satisfies a conservation law (2.3), and can be interpreted as the probability density of a particle in space. The conservation law follows from Schrödinger's

equation (1.1) with the Hamiltonian (1.2), as follows:

$$\begin{aligned}
\frac{\partial}{\partial t} \psi^\dagger \psi &= \psi^\dagger \frac{\partial \psi}{\partial t} + \frac{\partial \psi^\dagger}{\partial t} \psi \\
&= \frac{1}{i\hbar} \left[\psi^\dagger (H\psi) - (H\psi)^\dagger \psi \right] \\
&= \frac{1}{i\hbar} \left\{ \psi^\dagger \left[\left(\frac{p^2}{2m} + V \right) \psi \right] - \left[\left(\frac{p^2}{2m} + V \right) \psi \right]^\dagger \psi \right\} \\
&= \frac{i\hbar}{2m} \left[\psi^\dagger (\nabla^2 \psi) - (\nabla^2 \psi^\dagger) \psi \right] \\
&= \frac{i\hbar}{2m} \nabla \cdot \left[\psi^\dagger (\nabla \psi) - (\nabla \psi^\dagger) \psi \right] \\
&= -\nabla \cdot \left[\psi^\dagger \left(\frac{\mathbf{p}}{2m} \psi \right) + \left(\psi^\dagger \frac{\mathbf{p}^\dagger}{2m} \right) \psi \right] \\
&= -\nabla \cdot \frac{1}{2} \left[\psi^\dagger (\mathbf{v} \psi) + (\psi^\dagger \mathbf{v}^\dagger) \psi \right] , \tag{2.1}
\end{aligned}$$

where \mathbf{v} is the velocity operator

$$\mathbf{v} \equiv \frac{\mathbf{p}}{m} = -\frac{i\hbar}{m} \frac{\partial}{\partial \mathbf{x}} . \tag{2.2}$$

Note that, by the definition of Hermitian conjugate as a transpose, the Hermitian conjugate operators such as \mathbf{p}^\dagger and \mathbf{v}^\dagger in equations (2.1) and (2.4) operate to the left. Equation (2.1) takes the form of a conservation law for the probability $\psi^\dagger \psi$

$$\frac{\partial}{\partial t} \psi^\dagger \psi + \nabla \cdot \mathbf{j} = 0 , \tag{2.3}$$

where the probability current density \mathbf{j} is

$$\mathbf{j} = \frac{1}{2} (\psi^\dagger \mathbf{v} \psi + \psi^\dagger \mathbf{v}^\dagger \psi) . \tag{2.4}$$

3. ONE-DIMENSIONAL MOTION

The Hamiltonian for one-dimensional motion of a particle of mass m moving in time-independent potential $V(x)$ is, equation (1.2),

$$H = \frac{p^2}{2m} + V(x) , \tag{3.1}$$

where $p = -i\hbar \partial / \partial x$ is the momentum operator in one dimension. The time-independent Schrödinger equation (1.6)

$$H\phi = E\phi \tag{3.2}$$

then becomes an eigenvalue equation

$$\frac{\partial^2 \phi}{\partial x^2} - \frac{2m}{\hbar^2} [V(x) - E] \phi = 0 \tag{3.3}$$

for the stationary states $\phi(x)$ and the energy E .

4. MOTION IN A SPHERICALLY SYMMETRIC FIELD

The Hamiltonian for a single particle of mass m moving in a time-independent, spherically symmetric, three-dimensional potential $V(r)$ is

$$H = \frac{p^2}{2m} + V(r) . \quad (4.1)$$

The square $p^2 = -\hbar^2 \nabla^2$ of the momentum operator $\mathbf{p} \equiv -i\hbar \nabla$ can be written as the sum of radial and angular parts

$$p^2 = p_r^2 + \frac{L^2}{r^2} , \quad (4.2)$$

where the radial momentum operator p_r is

$$p_r \equiv -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r , \quad (4.3)$$

with square

$$p_r^2 = -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} . \quad (4.4)$$

It is not hard to determine that the angular momentum operator \mathbf{L} commutes with both the radial operator r and its derivative $r\partial/\partial r = \mathbf{r} \cdot \partial/\partial \mathbf{r}$, and also with L^2 ,

$$[\mathbf{L}, r] = 0 , \quad [\mathbf{L}, \mathbf{r} \cdot \mathbf{p}] = 0 , \quad [\mathbf{L}, L^2] = 0 , \quad (4.5)$$

and thence to conclude that \mathbf{L} commutes with all the terms of the spherically symmetric Hamiltonian (4.1)

$$[\mathbf{L}, H] = 0 . \quad (4.6)$$

According to the general principle, this means that angular momentum (about the center of mass) is conserved, a not unexpected conclusion for a spherically symmetric potential. Now \mathbf{L} does not commute with itself, so the three components of \mathbf{L} are not separately conserved. However, the square L^2 and component L_z in some arbitrary direction $\hat{\mathbf{z}}$ form a complete set of commuting operators for angular momentum. Thus a complete set of commuting operators for motion in a spherical symmetric potential is

$$H , \quad L^2 , \quad L_z , \quad (4.7)$$

with eigenvalues

$$E , \quad l(l+1)\hbar^2 , \quad m\hbar . \quad (4.8)$$

It follows that there exist wavefunctions which are products of a radial part $R(r)$ and an angular part $Y_{lm}(\hat{\mathbf{r}})$

$$\phi(\mathbf{r}) = R(r)Y_{lm}(\hat{\mathbf{r}}) . \quad (4.9)$$

The radial part $R(r)$ satisfies the eigenvalue equation

$$\left[\frac{1}{2m} \left(p_r^2 + \frac{l(l+1)\hbar^2}{r^2} \right) + V(r) - E \right] R(r) = 0 , \quad (4.10)$$

or equivalently

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2} [V(r) - E] \right] R = 0 . \quad (4.11)$$

With the substitution

$$R(r) = \chi(r)/r , \quad (4.12)$$

the radial equation (4.11) becomes

$$\frac{d^2\chi}{dr^2} - \left[\frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}[V(r) - E] \right] \chi = 0 , \quad (4.13)$$

which looks like the Schrödinger equation for one-dimensional motion of a particle, equation (3.1), in an effective potential

$$V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2mr^2} + V(r) . \quad (4.14)$$

The effective potential $V_{\text{eff}}(r)$ is the sum of the potential $V(r)$ with a repulsive centrifugal potential proportional to $1/r^2$. For bound state wavefunctions, unit normalization of the wavefunction $\int \phi^\dagger \phi d^3r = 1$ is accomplished by

$$\int_0^\infty |R|^2 r^2 dr = \int_0^\infty |\chi|^2 dr = 1 . \quad (4.15)$$

5. THE TWO-BODY PROBLEM

The problem of two nonrelativistic particles, masses m_1 and m_2 , interacting through a potential energy $V(r)$ which depends only on the separation r between the two particles can be reduced, as in classical mechanics, to the problem of a single particle of reduced mass $m = m_1 m_2 / (m_1 + m_2)$ moving in a spherically symmetric potential $V(r)$. The two-particle Schrödinger equation is

$$H\phi(\mathbf{r}_1, \mathbf{r}_2) = E\phi(\mathbf{r}_1, \mathbf{r}_2) , \quad (5.1)$$

with Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(r) , \quad (5.2)$$

where $\mathbf{p}_i \equiv -i\hbar\partial/\partial\mathbf{r}_i$ are the respective momenta of the two particles. In terms of the separation vector \mathbf{r} and center of mass vector \mathbf{R} ,

$$\mathbf{r} \equiv \mathbf{r}_2 - \mathbf{r}_1 , \quad \mathbf{R} \equiv \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} , \quad (5.3)$$

the Hamiltonian (5.2) becomes

$$H = \frac{P^2}{2M} + \frac{p^2}{2m} + V(r) , \quad (5.4)$$

where $\mathbf{P} \equiv -i\hbar\partial/\partial\mathbf{R}$ and $\mathbf{p} \equiv -i\hbar\partial/\partial\mathbf{r}$ represent the momenta of the motion of the center of mass and of the relative motion of the particles, and $M \equiv m_1 + m_2$ and $m \equiv m_1 m_2 / (m_1 + m_2)$ are the total and reduced mass. The Hamiltonian (5.4) is the sum of a part $P^2/(2M)$ which describes the free motion of the center of mass as a particle of mass M , and a part $p^2/(2m) + V(r)$ which is equivalent to one-dimensional motion of a particle of mass m in a spherically symmetric field $V(r)$.

It is apparent that \mathbf{P} commutes with the Hamiltonian

$$[\mathbf{P}, H] = 0 , \quad (5.5)$$

so that the momentum of the center of mass is conserved, as might be expected. The two-particle wavefunction can be written as the product

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{\text{free}}(\mathbf{R})\phi(\mathbf{r}) \quad (5.6)$$

of a wavefunction $\phi_{\text{free}}(\mathbf{R})$ which describes the free motion of the center of mass, with a wavefunction $\phi(\mathbf{r})$ which describes the relative motion of the particles.

6. COULOMB UNITS AND ATOMIC UNITS

The attractive Coulomb potential is

$$V(r) = -\frac{C}{r}, \quad (6.1)$$

where C is some constant. A **hydrogenic**, or **H-like**, atom is an atom having a single electron orbiting a nucleus of charge Z . In the nonrelativistic approximation, the potential $V(r)$ of a hydrogenic atom is the Coulomb potential (6.1) with

$$C = Ze^2. \quad (6.2)$$

Schrödinger's equation for a particle mass m moving in the spherically symmetric Coulomb potential (6.1) is characterized by three dimensional constants, which are m , \hbar , and C . In the hydrogenic atom, these constants are the reduced mass $m = m_e m_i / (m_e + m_i)$, \hbar , and Ze^2 . If the nuclear mass m_i is large compared to the electronic mass m_e , then $m \approx m_e$ to a good approximation, but this is not invariably the case — for example, positronium, in which a positron and electron temporarily form a bound state, has a reduced mass $m = m_e/2$.

Units of mass, length and time in which $m = \hbar = C = 1$ are called **Coulomb units**, while units in which $m_e = \hbar = e = 1$ are called **atomic units**, often abbreviated a.u.

Property	Coulomb Unit	Atomic Unit	Value of a.u.
Mass	m	m_e	$9.109\,389\,7(54) \times 10^{-28}$ gm
Length	$\frac{\hbar^2}{mC}$	$a_0 \equiv \frac{\hbar^2}{m_e e^2}$	$0.529\,177\,249(24) \times 10^{-8}$ cm
Time	$\frac{\hbar^3}{mC^2}$	$\frac{\hbar^3}{m_e e^4}$	$2.418\,884\,34 \times 10^{-17}$ s
Velocity	$\frac{C}{\hbar}$	$\frac{e^2}{\hbar}$	$2.187\,691\,42 \times 10^8$ cm s ⁻¹
Energy	$\frac{mC^2}{\hbar^2}$	$\frac{m_e e^4}{\hbar^2}$	$4.359\,748\,2(26) \times 10^{-11}$ erg
Angular momentum	\hbar	\hbar	$1.054\,572\,66(63) \times 10^{-27}$ erg s

The atomic unit of length a_0 is called the **Bohr radius**. A **Rydberg** is half an atomic unit of energy,

$$1 \text{ Rydberg} = 1/2 \text{ a.u.} = \frac{m_e e^4}{2\hbar^2} = 2.179\,874\,1(13) \times 10^{-11} \text{ erg} = 13.605\,698\,1(40) \text{ eV}, \quad (6.3)$$

and is equal, modulo relativistic correction effects, to the ionization energy of H. The Coulomb unit of velocity in a hydrogenic atom, call it v_{atom} , can be written

$$v_{\text{atom}} \equiv \frac{Ze^2}{\hbar} = Z\alpha c, \quad (6.4)$$

where α is the dimensionless **fine-structure constant**

$$\alpha \equiv \frac{e^2}{\hbar c} = \frac{1}{137.0359895(61)}. \quad (6.5)$$

Thus the characteristic velocities of electrons in hydrogenic atoms, $v_{\text{atom}} \approx Zc/137$, are nonrelativistic for small Z , justifying a nonrelativistic treatment to lowest order. Relativistic effects become increasingly important as Z increases.

7. COULOMB, OR HYDROGENIC, WAVEFUNCTIONS

Since the Coulomb potential (6.1) is spherically symmetric, the wavefunctions of particles orbiting in such a potential can be separated into radial and angular parts

$$\phi(\mathbf{r}) = R(r)Y_{lm}(\hat{\mathbf{r}}). \quad (7.1)$$

In Coulomb units $m = \hbar = C = 1$, the radial part $R(r)$ of the Coulomb wavefunction satisfies, equation (4.12),

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2}{r} + 2E \right] R = 0. \quad (7.2)$$

The substitutions

$$x = \frac{2r}{n}, \quad E = -\frac{1}{2n^2}, \quad R = e^{-x/2} x^l w(x) \quad (7.3)$$

transform equation (7.2) into

$$\left[x \frac{d^2}{dx^2} + (2l+2-x) \frac{d}{dx} + (n-l-1) \right] w = 0, \quad (7.4)$$

which looks like Kummer's differential equation. The solutions which remain well-behaved at infinity (they do not blow up exponentially) are **Kummer functions**

$$w(x) \propto M(-n+l+1, 2l+1, x). \quad (7.5)$$

Kummer functions $M(a, b, x)$, also known as **confluent hypergeometric functions** ${}_1F_1(a, b, x)$, are defined by the series expansion

$$M(a, b, x) = {}_1F_1(a, b, x) = 1 + \frac{a}{b}x + \frac{a(a+1)}{b(b+1)} \frac{x^2}{2!} + \dots, \quad (7.6)$$

which converges for all finite (complex, in general) x , provided that b is not zero or a negative integer (unless a is zero or a negative integer, in which case b may be a negative integer less than a). If a is zero or a negative integer, then the series (7.6) terminates, and the Kummer functions reduce to polynomials. Up to a normalization constant and a fiddling around of

the indices, Kummer functions are also the same as **associated Laguerre functions**¹ (Abramowitz & Stegun 1972)

$$L_{\nu}^{\lambda}(x) = \frac{\Gamma(\nu + \lambda + 1)}{\Gamma(\nu + 1)\Gamma(\lambda + 1)} M(-\nu, \lambda + 1, x) . \quad (7.7)$$

If ν is zero or a positive integer, the associated Laguerre functions become the associated Laguerre polynomials.

For bound states, those with negative energy E , the radial Coulomb wavefunctions are, normalized per (4.15),

$$R_{nl}(x) = C_{nl} e^{-x/2} x^l L_{n-l-1}^{2l+1}(x) , \quad (7.8)$$

with normalization constants

$$C_{nl} = \frac{2}{n^2} \left[\frac{(n-l-1)!}{(n+l)!} \right]^{1/2} . \quad (7.9)$$

The radial wavefunctions converge exponentially at infinity provided that $n-l-1$ is zero or a positive integer (otherwise, the radial wavefunctions diverge exponentially), so that the radial quantum number n can take values

$$n = l+1, l+2, \dots . \quad (7.10)$$

The associated Laguerre polynomials $L_{\nu}^{\lambda}(x)$ can be evaluated using the stable recurrence relation

$$(\lambda + 1)(\nu + 1)(\nu + \lambda) L_{\nu+1}^{\lambda-2}(x) = \lambda [(\lambda - 1)(\lambda + 1) - (2\nu + \lambda + 1)x] L_{\nu}^{\lambda}(x) - (\lambda - 1)x^2 L_{\nu-1}^{\lambda+2}(x) \quad (7.11)$$

starting from

$$L_{-1}^{2n+1} = 0 , \quad L_0^{2n-1} = 1 . \quad (7.12)$$

The bound-state Coulomb wavefunctions can be extended into the continuum regime of unbound states by taking $n = -i/k$ to be imaginary. Thus the continuum Coulomb wavefunctions are proportional to Kummer functions of imaginary argument. Their numerical evaluation is more complicated than the bound wavefunctions.

¹Some authors use other notations. Landau & Lifshitz (1977) Quantum Mechanics and Shu (1991) use **generalized Laguerre functions** L_{ν}^{λ} (roman symbol L) related to the associated Laguerre functions L_{ν}^{λ} (italic symbol L) here by

$$L_{\nu+\lambda}^{\lambda}(x) = (-)^{\lambda} \Gamma(\nu + \lambda + 1) L_{\nu}^{\lambda}(x) .$$