

Key Concepts in Atomic, Molecular, and Optical Physics

PHYS 522: Introduction to Quantum Optics and Quantum Photonics

1 The Hydrogen Atom

The hydrogen atom is the simplest of all possible atoms and, in the formulation of quantum mechanics, admits closed-form solutions. However, before the advent of the quantum theory various models competed to explain the relation between atomic structure and the narrow spectral lines observed in spectroscopic analyses. At the time, the electron was thought to follow classical, circular orbits around the nucleus such as the planets in our Solar System. Although the model (known as the Rutherford Model) provided a qualitatively picture of the spatial extent of nucleus and its electrons, it fell short to capture the nature of the observed spectrums. It was Niels Bohr who, in 1913, provided an accurate explanation by extending the Rutherford model with three postulates:

- The classical equations of motion are valid for electrons in atoms. However, only certain orbits with discrete energies E_n are allowed.
- In these quantized orbits, the electrons do not radiate energy.
- Electrons can jump between discrete orbits by emitting or absorbing electromagnetic radiation of frequency equal to the two orbit's energy difference.

Following simple classical mechanics, Bohr found an explicit formula for the discrete energies of the electron, characterized by the quantum number n ,

$$E_n \approx -\frac{13.6}{n^2} [eV]. \quad (1)$$

The discrete energy levels predicted by Bohr were an excellent match with previous empirical and experimental results and, furthermore, correctly predicted yet-to-be observed spectral lines.

Although the Bohr theory was a great success in understanding the atomic structure of matter and its interaction with light, the theory failed to predict or explain several phenomena such as multi-electron energy levels, magnetic field induced

splitting, and relativistic electron motion. Additionally, Bohr's postulates could not be rigorously justified. It was not until the development of the Schrodinger's equation that several of these concerns were addressed.

1.1 The gross structure

In non-relativistic quantum mechanics, a single electron of mass m_e bound by the Coulomb potential of a proton of mass m_p has a Hamiltonian given by,

$$\hat{H} = \frac{\hat{\mathbf{p}}_p^2}{2m_p} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{x}}_p - \hat{\mathbf{x}}_e|}. \quad (2)$$

This two-body Hamiltonian reduces to a one-body, internal Hamiltonian when considering only the relative position of the electron with respect to the proton. In spherical coordinates the full Schrodinger equation becomes,

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) |\Psi(r, \theta, \phi)\rangle = E |\Psi(r, \theta, \phi)\rangle, \quad (3)$$

where coordinates (r, θ, ϕ) are the electron's relative radial distance, polar, and azimuthal angle, respectively, and m is the reduced mass, which we approximate as the mass of the electron.

Table 1 Hydrogen wave functions; a_0 is the Bohr radius.

n	l	m	$ \Psi(r, \theta, \phi)\rangle$
1	0	0	$\frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2}\pi a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/a_0}$
2	1	0	$\frac{1}{4\sqrt{2}\pi a_0^{3/2}} \frac{r}{a_0} e^{-r/a_0} \cos(\theta)$
2	1	± 1	$\frac{1}{8\sqrt{2}\pi a_0^{3/2}} \frac{r}{a_0} e^{-r/a_0} \sin(\theta) e^{\pm i\phi}$

The solution of Eq. 3 is given by the product of radial and angular wave functions, characterized by three quantum numbers (n, l, m) ,

$$|\Psi(r, \theta, \phi)\rangle = |R_{n,l}(r)\rangle |Y_{l,m}(\theta, \phi)\rangle. \quad (4)$$

Quantum number n is known as the *principal quantum number* and can take any integer value from 1 to ∞ . It determines the energy spectrum of hydrogen as is given exactly as predicted by Bohr in Equation 1. The quantum number l is associated with the orbital angular momentum of the electron and can take any integer value from 0 to $n - 1$. Lastly the projection of the orbital angular momentum vector onto the

z -axis is quantized in the integer quantum number m , which may take integer values from $-l$ to l . Although not explicitly determined by the non-relativistic Schrodinger equation, there is a fourth quantum number m_s . This is the intrinsic spin of the electron projected onto the z -axis and, for spin-1/2 particles such as an electron, the values are $\pm \frac{1}{2}$

1.2 Fine Structure

Although the Coulomb potential is the principal interaction within the hydrogen atom, lower order corrections are present. The strongest of these is termed the *fine structure* and is characterized by energy shifts of order α^2 ($\alpha \approx (1/137)$) smaller than the gross energy levels. The energy shifts arise from several mechanisms, the most important being the *spin-orbit interaction*. The Hamiltonian for this interaction is

$$\hat{H}_{so} = C \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (5)$$

where C is a coupling constant, and $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are the orbital angular momentum and spin of the electron, respectively. This Hamiltonian is generated from the dipole-dipole interaction between the magnetic dipole of the electron and the internal magnetic dipole of the electron. The energy shift due to this additional term is given by,

$$\Delta E_{so} = D[J(J+1) - L(L+1) - S(S+1)], \quad (6)$$

where J is the total angular momentum, i.e. $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$.

1.3 Hyperfine Structure

In addition to the fine structure corrections, there are additional terms which contribute to energy shifts of much smaller order; corrections at this level are called *hyperfine*. Similar to the dipole coupling between magnetic moments and internal moments, energy shifts are induced by the angular momentum coupling between the nuclear spin $\hat{\mathbf{I}}$ and the total angular momentum of the electron $\hat{\mathbf{J}}$. Given the total angular momentum $\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}}$, the energy shift is,

$$\Delta E_{HF} = A(J)[F(F+1) - J(J+1) - I(I+1)], \quad (7)$$

where AJ is a coupling factor. The energy splitting is typically in the range of 0.1 cm^{-1} .

1.4 Stark Effect

By applying an external field, the energy levels of an atom shift. In the case of an applied electric field, the electric dipole moment interacts with the applied electric field - this is called the *Stark Effect*. Typically the energy shift is distinguished between first and second order. The first order shift is linear in the applied field, while the second order shift is quadratic.

1.5 Zeeman Effect

In an analogous treatment, the magnetic moment of an atom can couple to an applied magnetic field. The strength of this interaction is $\Delta E_Z = -\hat{\mathbf{u}} \cdot \hat{\mathbf{B}}$ where $\mu = -g_J \mu_B M_J$ and g_J is the Lande g-factor given by,

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (8)$$

The energy splitting between various M_J is then,

$$\Delta E_Z = g_J \mu_B B_z M_J. \quad (9)$$

2 Atoms and the Periodic Table

2.1 Multi-electron Atoms

The great success of the Hydrogen atom is due to its exact solution. Unfortunately, this system is the only atom with a closed-form solution and multiple complications arise when considering atoms with more than one electron. These complications can be gleaned by considering the Hamiltonian of an atom or ion consisting of N electrons and an atomic nucleus of mass m_{nuc} and charge number Z :

$$\hat{H} = \frac{\hat{\mathbf{P}}_{nuc}^2}{2m_{nuc}} + \sum_{i=1}^N \left(\frac{\hat{\mathbf{P}}_{ei}^2}{2m_{ei}} - \frac{Ze^2}{4\pi\epsilon_0 |\hat{\mathbf{x}}_{ei} - \hat{\mathbf{x}}_{nuc}|} \right) + \sum_{i < j} \left(\frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{x}}_{ei} - \hat{\mathbf{x}}_{ej}|} \right) \quad (10)$$

This many-body problem poses a major challenge and is in general unsolvable. However, several methods exist for finding approximate solutions which are correct to a fair degree of accuracy.

Typically, as in the analysis of the hydrogen system, the Hamiltonian is decomposed into a center-of-mass term and an internal term. The internal term is then,

$$\hat{H} = \sum_{i=1}^N \left(\frac{\hat{\mathbf{p}}_i^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i<j} \left(\frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \right). \quad (11)$$

The last term in this Hamiltonian is the Coulomb electron-electron interaction and contributes significantly to the total energy of the system. However, it is reasonable to assume that the electrons in the valence shell see an effective nuclear potential which is screened due to closed-shell electrons. In this way, the e-e interaction term may be split into an effective spherically symmetric potential, which contributes to the nuclear screening, and a two-body term between the valence electrons. The approximation is then to neglect the valence electron mutual term - this is the *Central Field Approximation*, and has been both theoretically and experimentally justified for many atoms and ions.

The beauty of this approximation is the Hamiltonian uncouples to a sum of independent single-particle terms, each of which is just the interaction between an electron and a screened Coulomb potential. The single-electron eigenfunctions under the central field approximation may then be characterized by the same quantum numbers as for the Hydrogen atom i.e. $|\Psi(\hat{\mathbf{r}}_i)\rangle = |n, l, m_l, m_s\rangle$. Since the electrons are indistinguishable, the N-electron Hamiltonian is invariant under the permutation of any two electrons. This implies the eigenstates may be characterized by the "good" quantum numbers of the permutation operator which has eigenvalues of +1 (Symmetric) and -1 (Anti-symmetric). *Pauli's Principle* states that fermions only occur in totally anti-symmetric states. For a N-electron wave function under the central field approximation, this is achieved by writing the wave function as a Slater determinant which guarantees the anti-symmetric symmetrization:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix} \quad (12)$$

2.2 The Periodic Table

Having seen that, to an approximation, the N-electron wave function may be written as a product of independent electrons, each characterized by its own set of 4 quantum number, the Periodic Table can be quantitatively understood in terms of the ground state configurations. If we consider that the electrons will effectively see a screened radial symmetric, Coulomb potential, it is reasonable to assume that the energy levels of the electrons will follow a similar $\frac{1}{n^2}$ law. Thus the lowest energy electrons will begin to fill the n -levels starting from $n = 1$. Each n th-level is referred to as a *shell*. Similarly, as the orbital angular momentum increases, the electrons tend to be "thrown" away from the nucleus, increasing the electrons energy. Thus the electron will favor the $2l+1$ available states within a particular shell with the lowest value of l ; each l value is referred to as a sub-shell. It remains to discuss

the order of states with different m_l and m_s values. For atoms with more than one valence electron, the spins and orbital angular momentum sum together in various combinations to form the total angular momentum. Depending on the coupling between spin and orbital angular momentum, different values of J are more energetically favorable and will determine the ground state. In general, *Hund's Rules* determine the configuration of the ground state among various m_l and m_s states.

3 Molecules and Solids

As seen in the previous section, exact solutions in quantum mechanics for atoms are restricted to the hydrogen atom; however, by making careful and well-justified approximations, complex systems may be accurately analyzed. Molecules and solids in a quantum mechanical framework are no exceptions. For predicting molecular bonds between various atoms and ions, the main analytic tool is the *Variational Principle* which states that the expectation value with respect to any normalized wave function $|\psi\rangle$ of a time-independent Hamiltonian is always greater than the energy of the true ground state i.e.

$$E_{gs} \leq \langle \psi | \hat{H} | \psi \rangle . \quad (13)$$

The great practicality of this method lies in the arbitrary choice of normalized wave function. Although the exact wave function of a complicated molecule may be unknown, it suffices to choose a particular subspace of orthogonal wave functions which are known and write the full trial wave function as a linear combination spanned by the subspace. The coefficients of expansion and additional parameters set within the basis wave functions themselves may be taken as variable degrees which can be minimized at the end of the expectation value calculation. The amount of variables to minimize is unlimited and very accurate ground state wave functions and eigenvalues may be determined. By analyzing particular systems such as the H_2 bond, ground state wave functions constructively interfere with one another, and electrons pair up to form what is manifested as covalent bonds.

When molecules become densely packed together by sharing interlinking bonds, the electron orbitals overlap and interfere to form broad continuous energy bands. For periodic structured systems, the bands are discontinuous over a region of energy known as the band gap. Electrons existing in bands below this gap are referred to as *Valence electrons* while electrons above the band gap are *Conduction electrons*. The transition from valence to conduction band - and *Vice Versa* - is mediated by the absorption/loss of energy which must be greater than the band gap of the material. Several band gap energies are given in Table 2.

Semiconductor	E_g (eV)
InAs	0.35
Ge	0.66
Si	1.12
InP	1.34
GaAs	1.52
CdSe	1.8
AlAs	2.15
GaP	2.27
CdS	2.5

References

1. Fox, Mark (2006) Quantum Optics: An Introduction. Oxford University Press
2. Haken, H. and Wolf, H.C. (2005) The Physics of Atoms and Quanta. Springer
3. Griffiths, David J. (2005) Introduction to Quantum Mechanics. Pearson Education Inc.
4. Harald, Friedrich (2006) Theoretical Atomic Physics. Springer