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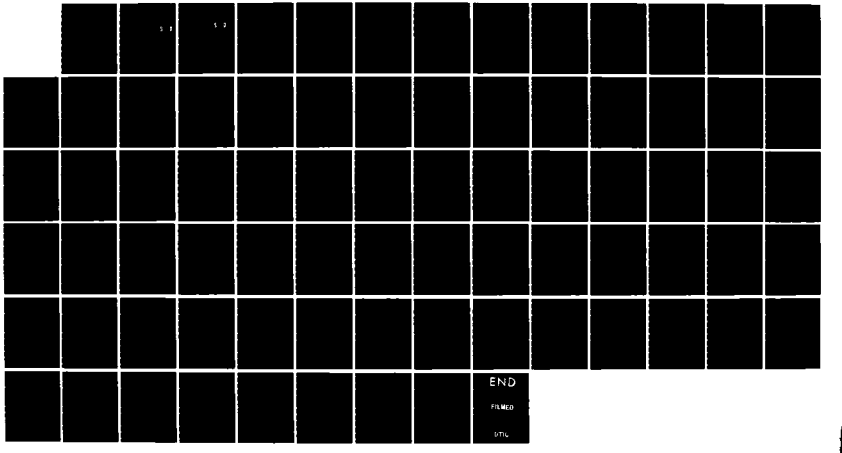

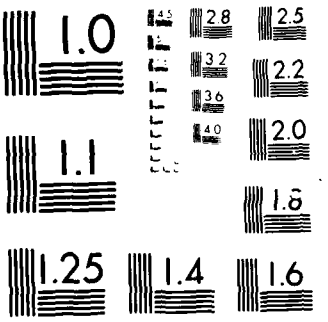

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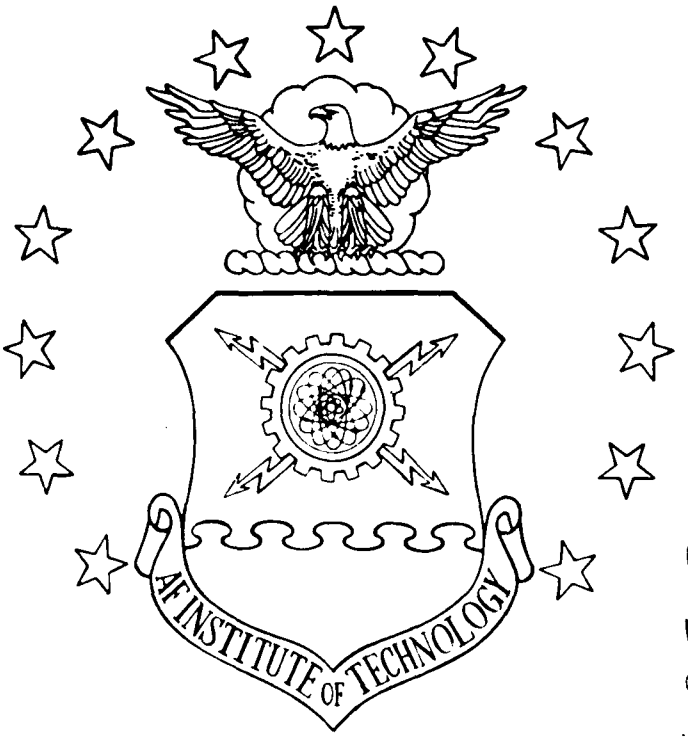

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THESIS

William Roc White
Captain, USAF

AFIT/GEP/PH/84D-13

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QUANTUM MECHANICAL ATOMIC ENERGY OPERATOR

THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering Physics

William Roc White, B.S.

Captain, USAF

December 1984

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Preface

The purpose of this thesis is to evaluate three possible choices of the atomic Hamiltonian as the energy operator for an atom in an electromagnetic field. Confusion between the Hamiltonian and the energy operator, and misinterpretation of operators in different representations have plagued student and author alike. Hopefully, this thesis will provide a document that can be used by others looking at the atomic energy operator or at various forms of the Hamiltonian, since there appears to be some confusion in the current literature. There are possible follow on studies suggested by the paper, primarily in experimental confirmation of the energy operator. The reader is expected to have had at least a first course in quantum mechanics.

I wish to sincerely thank Dr. Richard J. Cook for his patience and assistance during the completion of this thesis, and for originally suggesting the topic. I must complement him on his thorough comprehension of the subject, a portion of which he has passed on to me. Also, I extend my appreciation to Dr. Charles H. Townes for suggesting that a charged particle reacts equally to a longitudinal or transverse field. Further, it is difficult to sufficiently commend my wife Barbara for her support during the course of this program, and her patience during the long hours of study. Finally, I wish to thank Cascade for her understanding and constant companionship during my studies.

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Abstract

Various forms of the atomic Hamiltonian are examined as the energy operator for an atom in an electromagnetic field, using the semiclassical approach. The unperturbed Hamiltonian and the full atomic Hamiltonian have been favorite choices in the past, but these give different predictions if treated as the energy operator. The $\vec{A}\cdot\hat{p}$ versus $\hat{r}\cdot\vec{E}$ controversy is also examined and clarified. Both choices have conflicts with observations or physical laws. Gauge invariance and the Stark effect are considered. The multipole Hamiltonian is presented and argued as the correct energy operator. Calculations for three photon absorption in a two level atom, using time dependent perturbation theory, yield significant differences in the predictions for absorption rate and resonant frequency.

QUANTUM MECHANICAL ATOMIC ENERGY OPERATOR

I. Introduction

Background

In quantum mechanics, the state vector $|\psi\rangle$ describes a physical system, and contains all information that can be determined about that system. If the state vector is known for all time, then one can easily predict or explain observed physical phenomenon. A fundamental postulate of quantum mechanics is that the Schrodinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}(t)|\psi\rangle \tag{1.1}$$

governs the time evolution of the state vector, where $\hat{H}(t)$ is the Hamiltonian operator for the system. The solution of this equation provides much insight for atomic and molecular processes, particularly interactions with light. Unfortunately, the Schrodinger equation is difficult to solve, and has exact solutions for only a few simple cases. Generally, approximation methods, such as perturbation theory, are used to arrive at a solution which gives a satisfactory explanation to observations.

In the Schrodinger equation, the Hamiltonian generally represents the total energy of the system. The exact quantum mechanical form usually originates from the classical Hamiltonian. In atomic systems, the form of the Hamiltonian is

important for predictions, often through perturbation theory, of transition rates, lineshapes, multiphoton processes, and Stark shifts. Different choices for the Hamiltonian can result in significantly different predictions. The key question is which Hamiltonian actually represents the energy of the atom. This has been the source of a great debate and misconception within the scientific community.

Some confusion arises by the common treatment of the Hamiltonian and the energy operator as equivalent. In fact, these quantities are very different in quantum mechanics (1:326; 2). The energy operator represents an observable, so its expectation value is the same in any representation. In general, the Hamiltonian is not an observable. Under a transformation to another representation, it can describe something other than the energy. This subtle difference is important since the eigenstates of the energy operator represent the stationary states of the atom. Care must be taken when defining what form of the Hamiltonian is to be the energy, a physical quantity, in a particular representation. Its expectation value must be invariant under transformation.

For the interaction of light with matter, a central issue is which form of the Hamiltonian represents the true energy of the atom (or what is the form of the atomic energy operator). Historically, there have been two choices for the energy operator in the semiclassical treatment. Semiclassical refers to quantizing the atom, but treating the electromagnetic field classically. The unperturbed atomic

Hamiltonian,

$$\hat{H}_o = \frac{\hat{\bar{p}}^2}{2m} + V(\hat{\bar{r}}) \tag{1.2}$$

is most often used to represent the atom's energy, where $\hat{\bar{p}}$ is the canonical momentum operator and V is the coulomb potential due to the nucleus. Others use the full atomic Hamiltonian,

$$\hat{H} = \frac{1}{2m}\left(\hat{\bar{p}} - \frac{e}{c}\bar{A}(\hat{\bar{r}},t)\right)^2 + V(\hat{\bar{r}}) \tag{1.3}$$

where $\bar{A}$ is the vector potential and V is the total scalar potential. Each of these forms results in a different interaction Hamiltonian when the atom is in an electromagnetic field. The first results in the minimal coupling Hamiltonian, which, in perturbation theory, has transition matrix elements of the form $\langle n|\frac{e}{mc}\bar{A}\cdot\hat{\bar{p}}|m\rangle$, between states of the unperturbed atom. The latter yields the electric dipole Hamiltonian, which has matrix elements $\langle n|-e\hat{\bar{r}}\cdot\bar{E}|m\rangle$. The difference has caused a great deal of confusion as to which one to use or if there is indeed a difference.

For several years, the two forms were considered equivalent since they are related to one another through a unitary transformation (3). Lamb (4:268), however, noted that it is important to choose the correct form since there is a difference in the lineshape predictions. Because of the gauge dependence of $\bar{A}\cdot\hat{\bar{p}}$, he favors the $\hat{\bar{r}}\cdot\bar{E}$ form. On the

other hand, textbooks routinely expand the full Hamiltonian, Eq (1.3), and treat the $\bar{A}\cdot\hat{p}$ term as a pertubation (5:459; 6:400-401). It seems well stated by Worlock (7:1327) that, "the choice is largely dictated by taste and convenience." The $\hat{r}\cdot\bar{E}$ form is found to be more useful in atomic and molecular applications, where the $\bar{A}\cdot\hat{p}$ form is used for energy bands in crystals. For single photon resonant absorption, there is essentially no difference in the predicted rates; however, the two give different predictions for two-photon absorption (7; 8). Although it is evident that distinct differences exist, the primary matter of which equation represents the energy of the atom is still unresolved.

A further point of confusion is the apparent equivalence of the two forms under a unitary transformation. Several authors have shown that $\langle n|-\frac{e}{mc}\bar{A}\cdot\hat{p}|m\rangle$ and $\langle n|-e\hat{r}\cdot\bar{E}|m\rangle$ will yield the same results if properly interpreted (9; 10; 11). Under a unitary transformation, the basis states of a given representation change. Thus, even though the eigenstates in each case have the same form, they do not represent the same state. With this interpretation, the two forms are indeed equivalent. If the states were considered the same, the gauge dependence of $\bar{A}$ would cause the matrix to be gauge dependent. A change of gauge manifests itself as a unitary transformation, in such a way that the matrix is invariant, and the two forms are equivalent (12). While these arguments are essentially correct, they do not fully answer which form of the Hamiltonian represents the energy

of the atom.

Until the atomic energy operator is correctly identified, misinterpretation and confusion will face those studying or applying quantum mechanics to light and matter interactions. Journal articles still appear that have varying interpretations of the energy operator (8; 13; 14). Perhaps in previous work, where the field intensities were relatively small, the differences were unimportant. Now, with high power lasers available that can produce strong fields, the differences will have a much greater impact.

Thesis Objective

There is an obvious need for clarification on the exact form of the energy operator. Accurate predictions for several atomic processes depend on the correct choice. The primary objective of this thesis is to examine analytically possible choices for the energy operator of an atom in a time varying electromagnetic field. A second objective is to clarify the controversy over the equivalence of the $\overline{A}\cdot\hat{\overline{p}}$ and $\hat{\overline{r}}\cdot\overline{E}$ forms of the transition matrix elements. The second objective comes as a natural prerequisite of the first. The choices for the energy operator include the two already introduced, Eqs (1.2) and (1.3), but because of certain shortcomings of each, a third choice is presented. This is the multipole expansion form of the Hamiltonian,

$$\hat{H} = \frac{\hat{\overline{p}}^2}{2m} + V(\hat{\overline{r}}) - e\hat{\overline{r}}\cdot\overline{E} + \ldots \qquad (1.4)$$

where the terms beyond the unperturbed part are the energy of an electric and magnetic multipole. This is an infinite series, but for practical applications, it is truncated to a few terms. Here only the electric dipole term is considered, but in those instances where the magnetic dipole or electric quadrapole is important, the corresponding terms should be included. Treatment of the multipole expansion form as the atomic energy operator has as of yet been unexplored.

It is quite clear that due to the extensive nature of the controversy, the only true test of a particular form of the energy operator is ultimately to be confirmation by experiment. As part of arguments for the multipole form, this thesis details calculations for a three-photon absorption experiment. There are significant differences between the predictions of the three possible energy operators. Final proof of this thesis will have to wait for such an experiment to be performed, but the objective of examining possible choices of the atomic energy operator is met.

Assumptions

The thesis considers the semiclassical approach in the analysis, for reasons of simplicity. The full quantum approach is deemed unnecessary for the arguments presented, and would significantly increase the complexity. In addition, only the electric dipole term of the multipole expansion is considered. The magnetic dipole or electric quadrapole terms could easily be incorporated into the model, if necessary.

For ease of notation, the bra-ket convention is used throughout.

The experimental calculations use a general two level system as its model. Several physical systems can be approximated as a two level system, with good results. The perturbation calculations become manageable with this assumption. Finally, in the calculations, the effects of spontaneous emission is ignored. Again, this serves to reduce the difficulty without hampering the arguments.

General Approach

The second thesis objective is to clarify the controversy between the unperturbed Hamiltonian, Eq (1.2), and the full atomic Hamiltonian, Eq (1.3). Chapter II discusses the origin and application of the two Hamiltonians. Emphasis is on the different set of basis states each defines when considered as the energy operator. The matter of the equivalence of the transition matrices is also covered here.

Chapter III addresses the shortcomings of the first two choices for the energy operator. The true energy operator must be gauge invariant and must account for the Stark effect for both longitudinal and transverse fields. Considering the unperturbed Hamiltonian as the energy operator results in gauge dependent predictions, and it does not show a Stark shift. The full atomic Hamiltonian has a Stark shift only for a longitudinal field, which violates special relativity.

The multipolar Hamiltonian is presented in Chapter IV. The justification is based on the classical multipole potential and that the Hamiltonian produces the correct Lorentz force in the classical limit. The Hamiltonian is gauge invariant and has a Stark shift for the total field. Finally, the transition matrix elements have a much different form than the previous cases, which should result in new predictions.

Chapter V contains a perturbation analysis of the three cases for three photon absorption. The calculations show order of magnitude differences in the absolute rates, and shifted resonant frequencies. These results provide a possible means to experimentally confirm the correct energy operator.

II. Historical Controversy

Origin of the Hamiltonians

Classically, the Hamiltonian of an isolated single electron atom is represented by the sum of the electron's kinetic and potential energy. In the quantum formalism, the physical quantities are replaced by operators to arrive at

$$\hat{H}_o = \frac{\hat{p}^2}{2m} + V(\hat{r}) \tag{2.1}$$

the unperturbed Hamiltonian. $\hat{p}$ is the canonical momentum operator, $-i\hbar\nabla$, and V is the coulomb potential due to the nucleus, $-\frac{e^2}{r}$. $\hat{H}_o$ defines a complete set of basis states through the time independent Schrodinger equation,

$$\hat{H}_o|n\rangle = E_n|n\rangle \tag{2.2}$$

$|n\rangle$ are the basis vectors which can describe the state vector:

$$|\psi\rangle = \sum_n a_n|n\rangle \tag{2.3}$$

Each of the basis states is also called a stationary state, and E_n represents the energy of that state. Most authors use these basis states for calculations of transition rates, and E_n as the energy levels of the atom. This method, which

will be covered later, is the simplest approach.

When the atom interacts with an electromagnetic field, the total Hamiltonian must now include this interaction. The most common representation of this Hamiltonian is again derived from classical arguments. The nonrelativistic Lagrangian for a single electron in an electromagnetic field is

$$L = \frac{mv^2}{2} - e\phi + \frac{e}{c}\bar{A}\cdot\bar{v} \tag{2.4}$$

where $\phi(\bar{r},t)$ and $\bar{A}(\bar{r},t)$ are the scalar and vector potentials (15:222). The canonical momentum is then

$$p_i = \frac{\partial L}{\partial V_i} = mv_i + \frac{e}{c}A_i \tag{2.5}$$

The Hamiltonian is defined by

$$H = \sum_i P_i V_i - L \tag{2.6}$$

which reduces to

$$H = \frac{1}{2m}\left(\bar{p} - \frac{e}{c}\bar{A}\right)^2 + e\phi \tag{2.7}$$

By using operators in place of the physical quantities, the quantum mechanical form of the total Hamiltonian emerges:

$$\hat{H} = \frac{1}{2m}\left(\hat{\bar{p}} - \frac{e}{c}\bar{A}(\hat{\bar{r}},t)\right)^2 + e\phi(\bar{r},t) \qquad (2.8)$$

In the semiclassical treatment, the field variables remain as C-numbers. The scalar potential here is the total scalar potential, which includes the coulomb potential of the nucleus.

The primary justification for using Eq (2.8) as the total Hamiltonian is that the equation of motion for the position operator has a form that corresponds to the classical Lorentz force (6:178-179). Using the Heisenberg equation of motion,

$$\frac{d\hat{x}_i}{dt} = \frac{1}{i\hbar}\left[\hat{x}_i,\hat{H}\right] = \frac{1}{m}\left(\hat{p}_i - \frac{e}{c}A_i\right) \qquad (2.9a)$$

$$\frac{d\hat{p}_i}{dt} = \frac{1}{i\hbar}\left[\hat{p}_i,\hat{H}\right] = -\frac{\partial\hat{H}}{\partial\hat{X}_i} \qquad (2.9b)$$

The brackets refer to commutation. From these relations, in a non-trivial derivation, the results become

$$\frac{d^2\hat{\bar{r}}}{dt^2} = e\bar{E} + \frac{1}{2}\frac{e}{c}\left(\frac{d\hat{\bar{r}}}{dt} \times \bar{B} - \bar{B} \times \frac{d\hat{\bar{r}}}{dt}\right) \qquad (2.10)$$

where

$$\bar{E} = -\nabla\phi - \frac{1}{c}\frac{\partial\bar{A}}{\partial t} \qquad (2.11a)$$

$$\bar{B} = \nabla \times \bar{A} \tag{2.11b}$$

Perturbation Theory

In most applications, the Schrodinger equation is impossible to solve exactly, so approximation methods are often used. A common method for time dependent Hamiltonians is perturbation theory, in which the total Hamiltonian is put in the form of an unperturbed Hamiltonian and a perturbation term:

$$\hat{H} = \hat{H}_o + \hat{H}_I \tag{2.12}$$

The unperturbed Hamiltonian satisfies the time independent Schrodinger equation, resulting in a set of basis states.

$$\hat{H}_o|n\rangle = E_n|n\rangle \tag{2.13}$$

The set of basis states represents the stationary states of the atom, and depends heavily on the choice for $\hat{H}_o$. The state vector or wave function is then expanded in terms of these basis states:

$$\psi = \sum_n a_n(t)|n\rangle\, e^{-iE_n t/\hbar} \tag{2.14}$$

The time dependent coefficients, $a_n(t)$, are interpreted such that $P_n = |a_n|^2$ is the probability of being in state $|n\rangle$.

Substituting Eq (2.14) into the Schrodinger equation, (1.1), and making use of Eq (2.13),

$$\dot{a}_n(t) = \frac{1}{i\hbar}\sum_m \langle n|\hat{H}_I|m\rangle\ a_m(t)e^{i\omega_{nm}t} \qquad (2.15)$$

where $\omega_{nm} = (E_n - E_m)/\hbar$. These equations define the time evolution of the state vector in terms of the a_n coefficients. The matrix element $\langle n|\hat{H}_I|m\rangle$ represents the transition from state $|m\rangle$ to state $|n\rangle$.

The transition process depends heavily on the interaction Hamiltonian and the precise eigenstates chosen as the basis. Special care must be taken in this latter point. Ideally, and what is most often assumed, is that the basis states represent the true energy eigenstates of the atom, and the eigenvalues E_n are the true energy of the states. The Hamiltonian chosen to represent the energy of the atom, $\hat{H}_o$ in this case, determines the basis states. It also determines the form of the interaction Hamiltonian. The scientific community appears to be split over which form of the Hamiltonian to use as the energy operator. The two major choices are the unperturbed Hamiltonian $\hat{H}_o$, Eq (2.1), and the full atomic Hamiltonian $\hat{H}$, Eq (2.8). They each yield a different set of eigenstates and a different interaction Hamiltonian.

$\hat{H}_o$ as the Energy Operator

If the unperturbed Hamiltonian is the energy operator, then the energy eigenstates satisfy

$$\hat{H}_o|n\rangle = E_n|n\rangle \tag{2.16}$$

Expanding the total Hamiltonian, Eq (2.8), for an atom in an electromagnetic field,

$$\hat{H} = \frac{\hat{p}^2}{2m} + e\phi \; - \frac{e}{mc}\,\bar{A}\cdot\hat{\bar{p}} + \frac{e^2}{2mc^2}\,A^2 \tag{2.17}$$

assuming that $\bar{A}$ can be considered constant over the extent of the atom, so that $\bar{A}$ and $\hat{\bar{p}}$ commute. This is the electric dipole approximation. Note that $\bar{A}(t)$ still varies with time, and the potential ϕ is the coulomb potential of the nucleus. The interaction Hamiltonian is then

$$\hat{H}_I = -\frac{e}{mc}\,\bar{A}\cdot\hat{\bar{p}} + \frac{e^2}{2mc^2}\,A^2 \tag{2.18}$$

The expanded form of the Schrodinger Eq (2.15) becomes

$$\dot{a}(t) = \frac{1}{i\hbar}\sum_m \langle n|\, -\frac{e}{mc}\,\bar{A}\cdot\hat{\bar{p}} + \frac{e^2}{2mc^2}\,A^2\,|m\rangle a_m e^{i\omega_{mn}t} \tag{2.19}$$

The A^2 term in the transition matrix adds a common phase to the amplitudes a_n ; thus, it can be ignored. Most texts disregard the term since it is small compared to the $\bar{A}\cdot\hat{\bar{p}}$

term (6:400). The transition matrix reduces to $\langle n | -\frac{e}{mc} \bar{A} \cdot \hat{\bar{p}} | m \rangle$; this is the minimal coupling interaction form.

The $\bar{A} \cdot \hat{\bar{p}}$ form of the transition matrix is commonly used in calculations to predict transition rates, lineshapes, etc. The basis states, $|n\rangle$, are assumed to be the eigenstates of the energy operator, $\hat{H}_o$ in this case, and the transitions are between these states. However, one obvious issue arises. $\bar{A}$ is the vector potential, which is not unique for a given electromagnetic field. A different choice of potentials,

$$\bar{A}' = \bar{A} + \nabla G \qquad \phi' = \phi - \frac{1}{c} \frac{\partial G}{\partial t} \tag{2.20}$$

where $G(\bar{r},t)$ is an arbitrary function, yield the same $\bar{E}$ and $\bar{B}$ fields, according to Eq (2.11). These gauge transformations do not alter physical quantities, but transforming $\bar{A}$, in this case, changes the value of the transition matrix. The interpretation of the matrix elements as representing transitions between the energy eigenstates results in gauge dependent predictions, although this is a common practice in calculations.

$\hat{H}$ as the Energy Operator

Another choice for the energy operator is the full atomic Hamiltonian, Eq (2.8). This defines a different set of basis states which are time dependent, since the Hamiltonian is

time dependent:

$$\hat{H}(t)\,|n(t)\rangle = E_n\,|n(t)\rangle \tag{2.21}$$

It will be shown that the energy eigenvalues are constant and equal to the eigenvalues of the unperturbed Hamiltonian.

To justify use of the full Hamiltonian as the energy operator consider an energy operator equal to the sum of the potential and kinetic energies

$$\hat{E} = \frac{1}{2}\, m\hat{v}^2 + V(\hat{\bar{r}}) \tag{2.22}$$

In an electromagnetic field, $\hat{\bar{v}} = \frac{1}{m}\left(\hat{\bar{p}} - \frac{e}{c}\,\bar{A}\right)$ and $V(\hat{\bar{r}}) = e\phi$, which upon substitution, is Eq (2.8).

The eigenstates of the energy operator are derived by a unitary transformation, $\hat{S}$, of the time independent Schrodinger equation. If $\hat{H}$ does indeed represent the energy of the atom, then the eigenvalues are unchanged in the transformation, and Eq (2.21) transforms as

$$\hat{H}'\,|n\rangle^* = E_n\,|n\rangle^* \tag{2.23}$$

where

$$\hat{H}' = \hat{S}\,\hat{H}\,\hat{S}^{+} \tag{2.24}$$

$$|n\rangle^* = \hat{S}\,|n(t)\rangle \tag{2.25}$$

With the unitary transformation defined as

$$\hat{S} = \exp\left[- ie\hat{\vec{r}} \cdot \vec{A}(t)/\hbar c \right] \tag{2.26}$$

then

$$\hat{H}' = \frac{\hat{p}^2}{2m} + e\phi \tag{2.27}$$

$\hat{H}'$ has the same form as the unperturbed Hamiltonian, and has eigenstates $|n>^*$ that are of the same form as the previous case. However, the unitary transformation causes a change of representation, so the new eigenstates are the same as the unperturbed states. The true energy eigenstates are $|n(t)>$, which are related to the unperturbed eigenstates by

$$|n(t)> = \hat{S}^+ |n>^* \tag{2.28}$$

Again, the energy eigenvalues are the same, which can cause some confusion, but $\hat{H}$ and $\hat{H}_o$ result in very different sets of energy eigenstates.

Choice of $\hat{H}$ as the energy operator also results in different physical predictions. Expanding the state vector in terms of the energy eigenstates,

$$|\psi(t)> = \sum_m c_n(t) |n(t)> e^{-iE_n t/\hbar} \tag{2.29}$$

Substituting Eq (2.29) into the Schrodinger equation,

$$\dot{C}_n(t) = -\sum_m \langle n(t) | \frac{\partial}{\partial t} | m(t) \rangle C_m(t) e^{i\omega_{mn}t} \tag{2.30}$$

Using Eq (2.28) this becomes

$$\dot{C}_n(t) = \frac{1}{i\hbar} \sum_m {}^*\langle n| - e\hat{\bar{r}} \cdot \bar{E} | m\rangle {}^* C_m e^{i\omega_{mn}t} \tag{2.31}$$

The position operator has the same form in both representations, since it is unaffected by the unitary transformation. The transition matrix can then be written as $\langle n| -e\hat{\bar{r}} \cdot \bar{E} | m\rangle$, where the eigenstates are those of the unperturbed Hamiltonian. This is the electric dipole interaction form.

The Schrodinger equation for the two Hamiltonians, Eqs (2.19) and (2.31), have the same form except for the matrix elements, or more specifically, the interaction Hamiltonians. In both cases, the matrix elements are calculated with the unperturbed eigenstates, even though they are different than the energy eigenstates for $\hat{H}$. The minimal coupling form is gauge dependent in this interpretation, due to its dependence on the vector potential $\hat{A}$. On the other hand, the electric dipole form is a function of the electric field, which is gauge invariant. If the matrix elements are to describe some physical process, the value cannot depend on the gauge. This demonstrates a clear difference between these two forms of the energy operator. Unfortunately, there is

still much confusion since the two forms are related by a unitary transformation. In quantum mechanics, physical predictions are not altered by unitary transformations; thus, the two forms have been considered equivalent. Yet, it is obvious that there is a difference. This problem deserves some investigation due to the wide spread misuse of this equivalence.

Equivalence of $\bar{A}\cdot\hat{\bar{p}}$ and $\hat{\bar{r}}\cdot\bar{E}$

Several authors have addressed the equivalence of the $\bar{A}\cdot\hat{\bar{p}}$ and $\hat{\bar{r}}\cdot\bar{E}$ forms of the transition matrix (3; 9; 11; 12), but due to widespread misinterpretation and its relevance to this thesis, it deserves mention here. The main problem is in the interpretation of the "unperturbed" basis states in each transition matrix.[9] It is assumed that both refer to the same set of basis states, but this is not the case. The numerical values are the same, but they are states in two different representations.

Consider first the full atomic Hamiltonian, Eq (2.8),

$$\hat{H} = \frac{1}{2m}\left(\hat{\bar{p}} - \frac{e}{c}\bar{A}\right)^2 + e\phi \qquad (2.32)$$

In this equation, $\hat{\bar{p}}$ is the canonical momentum operator, not the kinetic momentum. The kinetic momentum is given by

$$m\hat{\bar{v}} = \left(\hat{\bar{p}} - \frac{e}{c}\bar{A}\right) \qquad (2.33)$$

Expanding Eq (2.32) in the electric dipole approximation,

$$\hat{H} = \frac{\hat{p}^2}{2m} + e\phi - \frac{e}{mc}\,\bar{A}\cdot\hat{\bar{p}} + \frac{e^2}{2mc^2}\,A^2 \tag{2.34}$$

The first two terms are in the form of $\hat{H}_o$, the unperturbed Hamiltonian, but the true unperturbed Hamiltonian differs in that the canonical momentum $\hat{\bar{p}}$ is also the kinetic momentum. Expanding on the basis states of $\hat{H}_o$ as before, the Schrodinger equation becomes

$$\dot{a}_n = \frac{i}{i\hbar}\sum_n \langle n|-\frac{e}{mc}\,\bar{A}\cdot\hat{\bar{p}}|m\rangle a_m e^{i\omega_{nm}t} \tag{2.35}$$

The electric dipole form of the Hamiltonian can be derived by applying the unitary transformation of Eq (2.26) to the Schrodinger equation. The Schrodinger equation becomes

$$i\hbar\,\frac{\partial}{\partial t}|\psi\rangle' = \hat{H}'|\psi\rangle' \tag{2.36}$$

where

$$|\psi\rangle' = \hat{S}|\psi\rangle \tag{2.37}$$

$$\hat{H}' = \hat{S}\,\hat{H}\,\hat{S}^{+} - i\hbar\hat{S}\,\frac{\partial\hat{S}}{\partial t} \tag{2.38}$$

Substituting Eq (2.32) into (2.38),

$$\hat{H}' = \frac{\hat{p}^2}{2m} + e\phi - e\hat{\bar{r}}\cdot\bar{E} \tag{2.39}$$

where $\bar{E}$ is given by $-1/c\ \partial\bar{A}/\partial t$. Again, the first two terms have the form of the unperturbed Hamiltonian. Expanding on the basis states of $\hat{H}_o$,

$$\dot{a}_n = \frac{1}{i\hbar} \sum_n \langle n|- e\hat{\bar{r}}\cdot\bar{E}|m\rangle\ a_m e^{i\omega_{nm}t} \tag{2.40}$$

Thus, it appears that Eqs (2.35) and (2.40) are identical except for the transition matrix. This misinterpretation has plagued scientists, and lured them to believe that it is equivalent to use either form (7:1327).

Upon careful examination, two mistakes emerge. In the unperturbed Hamiltonian of Eq (2.39), $\bar{p}$ actually represents the kinetic momentum, unlike the earlier case. Consider the unitary transformation of the kinetic momentum,

$$m\hat{\bar{v}}' = \hat{S}\ m\hat{\bar{v}}\ \hat{S}^+ = \hat{S}(\hat{\bar{p}} - \frac{e}{c}\bar{A})\hat{S}^+ \tag{2.41}$$

$\hat{S}$ and $\hat{\bar{A}}$ commute, but

$$\hat{S}\ \hat{\bar{p}} = \hat{\bar{p}}\ \hat{S} + i\hbar\ \frac{\partial\hat{S}}{\partial\hat{\bar{r}}}$$

$$= \hat{\bar{p}}\ \hat{S} + \frac{e}{c}\bar{A}\ \hat{S} \tag{2.42}$$

Thus,

$$\hat{m}\hat{v}' = \hat{p} \tag{2.43}$$

The basis states of Eq (2.40) are distinct from the those of Eq (2.35).

The second mistake involves the interpretation of the coefficients a_n . It was assumed that in both cases, a_n represents the expansion coefficients of the state vector on the unperturbed basis states. The transformation of the state vector must also transform the basis states. This is a mistake often made in the literature (13:625,631).

$$|\psi>' = \hat{S}|\psi> = \sum_n a_n \hat{S}|n> \tag{2.44}$$

Recall Eq (2.25)

$$|n(t)>' = \hat{S}|n> \tag{2.45}$$

Thus, in the second case, a_n are the expansion coefficients of the time dependent basis states.

Eqs (2.35) and (2.40) are indeed related to one another and can be considered equivalent if properly handled. Physical predictions will then be invariant in either case using the correct interpretation. Unfortunately, this still does not address the problem of the form of the atomic energy operator. The two possibilities still exist; the unperturbed Hamiltonian $\hat{H}_o$ or the full atomic Hamiltonian $\hat{H}$. A better

argument currently exists for $\hat{H}$, since treating $\hat{H}_o$ as the energy operator results the transition matrix involving $\bar{A}\cdot\hat{\bar{p}}$, which is gauge dependent.

III. Limitations of $\hat{H}_o$ and $\hat{H}$ as the Energy Operator

The correct choice of the energy operator must be consistent with experimental observations and physical laws. The results of physical predictions must be gauge invariant, since the choice of gauge is arbitrary. Observed phenomenon such as the Stark effect must also be accountable in the theory. Finally, the theory must be consistent with the theory of special relativity. Neither $\hat{H}_o$ nor $\hat{H}$ meet these requirements, and thus do not accurately represent the true energy.

Gauge Invariance

Electric and magnetic fields can be described in terms of the vector and scalar potentials, Eq (2.11). However, the potentials are not unique; a different set of potentials from Eq (2.20) yields the same fields. This demonstrates that the potentials are unphysical, and only the fields are important physically. An additional condition, a gauge condition, can be imposed on the potentials without affecting the outcome. An often used condition is the coulomb gauge:

$$\nabla \cdot \bar{A} = 0 \tag{3.1}$$

With this condition, the operators $\bar{A}$ and $\hat{\bar{p}}$ commute, and the electric field can conveniently be expressed in terms of its longitudinal and transverse components (16:125). The longitudinal component of a vector field, $\bar{V}$, is defined as

$$\nabla \times \overline{V}_L = 0 \tag{3.2}$$

The transverse component obeys

$$\nabla \cdot \overline{V}_T = 0 \tag{3.3}$$

The electric field, in coulomb gauge, is then $\overline{E} = \overline{E}_L + \overline{E}_T$, where

$$\overline{E}_L = - \nabla\phi$$

$$\overline{E}_T = - \frac{1}{c} \frac{\partial \overline{A}}{\partial t} \tag{3.4}$$

The magnetic field is always transverse:

$$\overline{B} = \overline{B}_T = \nabla \times \overline{A} \tag{3.5}$$

Expressing the full atomic Hamiltonian in this gauge is useful, although not necessary. Any accurate physical model does not depend on the gauge chosen for its predictions.

Since the full atomic Hamiltonian, Eq (2.8), depends on the potentials, its behavior under gauge transformations should be understood. The Schrodinger equation is form invariant under a gauge transformation (1:323-325), meaning that Eq (1.1) takes the same form in any gauge:

$$i\hbar \frac{d}{dt} |\psi\rangle' = \hat{H}'(t) |\psi\rangle'$$

$$\hat{H}' = \frac{1}{2m}\left(\hat{\bar{p}} - \bar{A}'(t)\right)^2 + e\phi'(t) \qquad (3.6)$$

Although $\hat{\bar{p}}$ does not change form in the new gauge, it represents a different quantity. Remember, $\hat{\bar{p}}$ is the canonical momentum, which is not a true observable. The change in $\hat{\bar{p}}$ results in a change in the basis states in the new representation if the eigenvectors of $\hat{H}_o$ are used.

A gauge transformation is equivalent to a unitary transformation to another representation (1:321), given by

$$\hat{U} = \exp\left[i \frac{e}{\hbar c} G(\hat{\bar{r}}, t)\right] \qquad (3.7)$$

where G is an arbitrary function which determines the gauge. For an operator, $\hat{T}$, to represent a physical quantity, the following condition must be met:

$$\hat{T}' = \hat{T}_u \equiv \hat{U}\ \hat{T}\ \hat{U}^+ \qquad (3.8)$$

where $\hat{T}'(\hat{\bar{A}}', \phi')$ is the operator in the new gauge, and $\hat{T}_u$ is the transformed operator. For example, consider the true momentum given by Eq (2.33),

$$m\hat{\bar{v}}' = (\hat{\bar{p}} - \frac{e}{c}\bar{A}') = (\hat{\bar{p}} - \frac{e}{c}\bar{A} - \frac{e}{c}\nabla G) \qquad (3.9)$$

$$m\hat{\bar{v}}_u = \hat{U}(\hat{\bar{p}} - \frac{e}{c}\bar{A})\hat{U}^+ = (\hat{\bar{p}} - \frac{e}{c}\nabla G - \frac{e}{c}\bar{A}) \qquad (3.10)$$

As expected, the true momentum is gauge invariant, $\hat{\bar{v}}' = \hat{\bar{v}}_u$. For a Hamiltonian, this is not generally true, unless it is the true energy operator of the atom.

If $\hat{H}_o$ is considered as the energy operator, then its exact meaning changes based on the interpretation of $\hat{\bar{p}}$ in the given representation. Even though the form remains the same, $\hat{H}_o$ is an unphysical quantity, as is $\hat{\bar{p}}$. $\hat{H}_o$ is gauge dependent in this manner. Another way to see this result is to consider the transition matrix element, $\langle n|\bar{A}\cdot\bar{p}|m\rangle$. The basis states are the energy eigenstates of $\hat{H}_o$, but $\bar{A}$ is gauge dependent. Thus, physical predictions become gauge dependent if $\hat{H}_o$ is treated as the energy operator.

Next consider the full atomic Hamiltonian, $\hat{H}$, as the energy operator. Again, the operator must be gauge invariant to represent a physical quantity. At first glance, the operator appears to be gauge dependent because of the gauge transformation of the scalar potential in $\hat{H}$:

$$\hat{H}' = \frac{1}{2m}(\hat{\bar{p}} - \frac{e}{c}\bar{A}')^2 + e\phi - \frac{e}{c}\frac{\partial G}{\partial t}$$

$$= \hat{H}_u - \frac{e}{c}\frac{\partial G}{\partial t} \qquad (3.11)$$

This is true only if the potential, ϕ , is the scalar potential. However, in the energy operator, the potential is actually the coulomb potential,

$$\phi = \sum_i \frac{q_i}{|\hat{\bar{r}} - \hat{\bar{r}}_i|} \tag{3.12}$$

which is gauge invariant since charge q and position $\bar{r}$ are invariant quantities. Hence, the Hamiltonian is also gauge invariant.

The total potential can be expressed as the sum of the potential due to the nucleus, ϕ_o , and that due to external sources, ϕ_{ext} ,

$$\phi = \phi_o + \phi_{ext} \tag{3.13}$$

The second term is then expanded with a Taylor series to arrive at a multipole expansion,

$$\begin{aligned} \phi_{ext} &= \phi(0) + \nabla\phi(0)\cdot\bar{r} + \ldots \\ &= \phi(0) - \bar{E}_L\cdot\bar{r} + \ldots \end{aligned} \tag{3.14}$$

Ignoring the constant, $\phi(0)$, and the higher order terms

$$\hat{H} = \frac{1}{2m}\left(\hat{\bar{p}} - \frac{e}{c}\bar{A}\right)^2 + e\phi_o - e\hat{\bar{r}}\cdot\bar{E}_L \tag{3.15}$$

Thus, the full atomic Hamiltonian is shown to be gauge invariant when handled in this way. Note also, that the transition matrix $\langle n|-e\hat{\bar{r}}\cdot\bar{E}|m\rangle$, which results from the choice of $\hat{H}$, is also gauge invariant, since it depends upon the electric field, and the states $|n\rangle$ are gauge invariant.

Stark Effect

The Stark effect is a shift in the atomic energy levels for an atom in an external electric field, and has been widely observed and reported. The true energy operator for the atom must reflect this energy shift. The unperturbed Hamiltonian contains no terms which include external fields; hence, its energy eigenstates are independent of the external fields. No Stark effect would be observed if $\hat{H}_o$ were the atomic energy operator. The external field would simply cause transitions between the eigenstates. The lack of a Stark shift is a strong argument against the unperturbed Hamiltonian as the energy operator.

The full Hamiltonian, Eq (3.15), includes the term $-e\hat{\bar{r}}\cdot\bar{E}_L$, so the energy eigenvalues are a function of the external field. Transforming the energy operator, Eq (3.15) with the unitary transformation of Eq (2.26),

$$\hat{H}' = \hat{S}\,\hat{H}\,\hat{S}^{+}$$

$$= \hat{H}_o - e\hat{\bar{r}}\cdot\bar{E}_L \qquad (3.16)$$

The energy eigenvalues of $\hat{H}'$, which are equal to those of $\hat{H}$, exhibit a dependence on the longitudinal portion of the electric field. The eigenvalues do not depend on the transverse component. A transverse field causes transitions between the eigenstates. This conclusion is, however, erroneous.

A charged particle cannot distinguish between the longitudinal and transverse portions of the electric field. If taken individually, the components are unphysical. Only the two combined together have a physical consequence. It would seem that the atom should then exhibit a Stark effect for both the longitudinal and transverse portions of the electric field.

The longitudinal electric field in coulomb gauge is

$$\bar{E}_L = -\nabla\phi = -\nabla \sum_i \frac{q_i}{|\hat{\bar{r}}-\hat{\bar{r}}_i|} \tag{3.17}$$

which is the instantaneous coulomb field. This shows the unphysical nature of $\bar{E}_L$, since an electric field travels at the speed of light, not instantaneously. If the Stark effect were dependent on the longitudinal field only, then there could be instantaneous knowledge of change in a charge distribution at a large distance, in violation of special relativity. Thus, the Stark effect must depend on the total electric field. In the total electric field, the unphysical portion of the transverse component cancels the unphysical

part of the longitudinal component, insuring that the field obeys special relativity (16:125; 17). The total Hamiltonian, which exhibits a Stark shift for only the longitudinal field, is then not the proper choice for the energy either.

Another Hamiltonian

The two choices normally considered for the energy operator have been shown to have some deficiencies. A strong argument exists against the unperturbed Hamiltonian because of its gauge dependence and lack of a Stark shift. The full Hamiltonian, although gauge invariant, shows a Stark shift for a longitudinal electric field only, which is in violation of special relativity. These arguments suggest that there must be yet another form of the Hamiltonian which represents the energy of the atom.

A reasonable choice is the full multipolar Hamiltonian, which consists of the unperturbed Hamiltonian plus the multipole energy expansion. In the electric dipole approximation, this is

$$\hat{H} = \frac{\hat{\bar{p}}^2}{2m} + V(\hat{\bar{r}}) - e\hat{\bar{r}} \cdot (\bar{E}_L + \bar{E}_T) \qquad 3.18)$$

This form reacts to both the longitudinal and transverse electric fields equally; thus, there is no violation of special relativity. In addition, if $V(\hat{\bar{r}})$ is the coulomb potential of the nucleus, the Hamiltonian is also gauge invariant. Thse topics are discussed in more detail in the next section.

IV. Multipole Hamiltonian as the Energy Operator

The Multipole Hamiltonian

The multipole form of the atomic Hamiltonian is usually derived from a unitary transformation of the full atomic Hamiltonian, Eq (2.8) (16:166-167; 18). The final result is

$$\hat{H} = \frac{1}{2m}\left[\hat{\bar{p}} - e\int_0^1 \lambda\hat{\bar{r}} \times \bar{B}(\lambda\hat{\bar{r}})\, d\lambda\right]^2$$

$$+ e\phi(\bar{r}) + e\int_o^1 \hat{\bar{r}} \cdot \bar{E}_T(\lambda\hat{\bar{r}})\, d\lambda \qquad (4.1)$$

where $\phi(\hat{\bar{r}})$ is the instantaneous coulomb potential due to the nucleus and any external charges. This Hamiltonian depends on the electric and magnetic fields instead of the potentials. Expanding the integrals and the potential, $\phi(\hat{\bar{r}})$, results in the convential multipole expansion. Note that the expansion of the potential contains the longitudinal electric field, $\bar{E}_L$; thus, the Hamiltonian depends on the total electric field.

It is the intent here to show justification for selecting Eq (4.1) as the energy operator based on the classical energy arguments and the requirements presented in the previous chapter. Detailed calculations for the full expansion are not included, since this thesis deals solely with the electric dipole portion for simplicity. The method can be extended to additional multipole terms as necessary.

Even though two Hamiltonians are unitarily related, it is conceivable that just one represents the energy operator. The interpretation of dynamical variables changes under a transformation (19), so the two Hamiltonians can mean very different things. Recall that under a unitary transformation, the Hamiltonian transforms as

$$\hat{H}' = \hat{S}\,\hat{H}\,\hat{S}^{+} - i\hbar\,\hat{S}\,\frac{\partial \hat{S}^{+}}{\partial t} \tag{4.2}$$

On the other hand, the energy operator transforms as

$$\hat{E}' = \hat{S}\,\hat{E}\,\hat{S}^{+} \tag{4.3}$$

If a Hamiltonian is the *energy operator* in one representation, the transformation of that Hamiltonian, under Eq (4.2), can represent something much different in another representation. This allows selection of Eq (4.1) as the energy operator despite the fact that it is unitarily related to Eq (2.8), which has been shown not to accurately represent the true energy of the atom.

For the derivation of the electric dipole form, consider the transformation of Eq (2.8) with the electric dipole approximation, where the vector potential $\bar{A}$ is a function of t only. The full Hamiltonian is

$$\hat{H} = \frac{1}{2m}\left(\hat{\bar{p}} - \frac{e}{c}\,\bar{A}(t)\right)^{2} + e\phi(\hat{\bar{r}}) \tag{4.4}$$

In Eq (4.2), let the unitary transformation be

$$\hat{S} = \exp\left[-\,i\,\frac{e}{\hbar c}\,\hat{\bar{r}}\cdot\bar{A}(t)\right] \tag{4.5}$$

Using the fact that $\hat{S}$ commutes with $\phi(\hat{\bar{r}})$ and $\bar{A}(t)$, and that

$$\left[\hat{\bar{p}},\hat{S}\right] = -\,i\hbar\,\frac{\partial\hat{S}}{\partial\hat{\bar{r}}} \tag{4.6}$$

the electric dipole form of the Hamiltonian becomes

$$\hat{H}' = \frac{\hat{\bar{p}}^2}{2m} + e\phi(\hat{\bar{r}}) - e\hat{\bar{r}}\cdot\bar{E}_T \tag{4.7}$$

where $\bar{E}_T = -\,\frac{\partial\bar{A}}{\partial t}$ is the transverse electric field in coulomb gauge. Expanding $\phi(\hat{\bar{r}})$, as in Eqs (3.13) and (3.14),

$$\hat{H}' = \frac{\hat{\bar{p}}^2}{2m} + e\phi_o - e\hat{\bar{r}}\cdot(\bar{E}_L + \bar{E}_T) \tag{4.8}$$

where ϕ_o is the coulomb potential of the nucleus. This is the dipole form of the multipole expansion; it contains both components of the electric field. Choosing Eq (4.8) as the energy operator is a different case than selecting the full atomic Hamiltonian, Eq (4.4).

To justify use of the multipole form of the Hamiltonian, consider the classical definition of energy, the sum of kinetic and potential energies. The kinetic energy can be

written as $p^2/2m$; in this case, $\bar{p} = m\bar{v}$. The potential energy of the electron depends on the coulomb potential of the nucleus, and the electromagnetic field:

$$V(\bar{r}) = e\phi_o + V_E + V_B \tag{4.9}$$

The potential energy of an electron in an electric field is given by the expansion (20:101)

$$V_E = e\,\phi(o) - e\bar{r} \cdot \bar{E}(o) - \frac{1}{6} \sum_i \sum_j Q_{ij} \frac{\partial E_j(o)}{\partial x_i} + \ldots \tag{4.10}$$

These are the monopole, dipole, and quadrapole terms of the electric multipole expansion. Q_{ij} is the quadrapole moment tensor. Similarly, the magnetic multipole energy can be expanded (20:148-150). For the magnetic dipole, $\bar{m}$,

$$V_B = - \bar{m} \cdot \bar{B} + \ldots \tag{4.11}$$

Thus, the total energy can be written as

$$E = \frac{p^2}{2m} + \left[e\phi - e\bar{r} \cdot \bar{E} - \ldots \right] + \left[- \bar{m} \cdot \bar{B} + \ldots \right] \tag{4.12}$$

This is of the same form of the multipole Hamiltonian, when operators are used in place of the physical quantities.

Based on these arguments, the Hamiltonian of Eq (4.8) is a reasonable choice for the energy operator in the electric dipole approximation. The electric dipole approximation is valid when the electric field has a negligible variation over the extent of the atom. If electric quadrapole or magnetic dipole interactions are important, then these terms should also be included in the Hamiltonian.

A further justification exists in the classical limit of the equation of motion, that results from this Hamiltonian.

$$\frac{d\hat{r}_i}{dt} = \frac{\hat{H}'}{\partial \hat{p}_i} = \frac{\hat{p}_i}{m} \tag{4.13a}$$

$$\frac{d\hat{p}_i}{dt} = -\frac{\partial \hat{H}'}{\partial \hat{x}_i} = e\frac{\partial \phi_o}{\partial \hat{x}_i} - e\frac{\partial}{\partial \hat{x}_i}(\hat{\bar{r}}\cdot\bar{E}) \tag{4.13b}$$

In the dipole approximation, $\bar{E} = \bar{E}(t)$, so

$$\frac{d^2\hat{\bar{r}}}{dt^2} = -\frac{e}{m}\bar{E} \tag{4.14}$$

which is the equation of motion for an electric field. Note that the gradient of the nuclear potential merely adds an additional electric field. If the full multipole expansion were used as the Hamiltonian, the proper Lorentz force law would result.

Gauge Invariance and Stark Effect

The energy operator, given by Eq (4.8), satisfies both the requirements of gauge invariance and a Stark shift for the total electric field. The Hamiltonian consists totally of gauge invariant quantities. The momentum operator represents the kinetic momentum. The potential is the coulomb potential of the nucleus. Finally, the electric dipole interaction term depends on the electric field, which is gauge invariant. In another gauge the Hamiltonian becomes

$$\hat{H}' = \frac{\hat{\bar{p}}^2}{2m} + e\phi_o - e\bar{r} \cdot \bar{E} = \hat{H}_u \qquad (4.15)$$

since $\hat{\bar{p}}' = \hat{\bar{p}}$ and $\hat{\bar{r}}' = \hat{\bar{r}}$. This differs from the previous case when $\hat{\bar{p}}$ transformed to $\hat{\bar{p}} - e\nabla G$, and $\hat{\bar{p}}$ was the canonical momentum given by $\hat{\bar{p}} = m\hat{\bar{v}} + \frac{e}{c}\bar{A}$.

In the interaction term, the electric field is the total field; thus, Stark shifts occur equally for either a longitudinal or transverse field. This prevents the violation of special relativity, as in the previous case. Furthermore, the Stark shift for a transverse field provides a possible means of experiemental confirmation of this Hamiltonian, if strong enough fields can be generated. The previous choices predicted no Stark shift for a transverse electric field, only transitions between eigenstates. The other terms of the multipole expansion allow shifts due to magnetic fields (the Zeeman effect), quadrapole fields, and so on.

With the new Hamiltonian expression for the energy operator, quantum descriptions of physical processes differ from the predictions of the previous two cases. One significant difference is that the energy operator is now a function of time, and can not be transformed to a time independent form. The eigenvalues will then be functions of time also. In the previous cases, the energy operator was either the unperturbed Hamiltonian, $\hat{H}_o$, or transformed to the form of $\hat{H}_o$, so the energy eigenvalues were constant. In the end, the differences in the predictions of the three Hamiltonians provide a means to determine the correct energy operator by correlation with experimental observations.

Dynamics of the Multipole Hamiltonian

For a time dependent Hamiltonia, the solution of the Schrodinger equation is not a stationary state. The expansion coefficients of the state vector are time dependent. When the multipole Hamiltonian is considered as the atomic energy operator, the energy eigenstates and eigenvalues are also functions of time. The resulting solution of the Schrodinger equation involves a state vector whose expansion coefficients and basis states are time dependent. In other words, the interaction with light causes both a shift in the energy states and transitions between the states.

In the electric dipole case, the Hamiltonian is

$$\hat{H}(t) = \frac{\hat{\bar{p}}^2}{2m} + e\phi_o(\hat{\bar{r}}) - e\hat{\bar{r}} \cdot \bar{E}(t) \qquad (4.16)$$

For optical frequencies and lower, the electric dipole form is sufficient since there is little variation of the electric field over the extent of the atom. The magnitude of the magnetic dipole term is a factor of $1/c$ smaller, so it can be ignored. Because $\hat{H}(t)$ is the energy operator, the energy eigenstates and eigenvalues satisfy the instantaneous time independent Schrodinger equation (6:289),

$$\hat{H}(t)\,|n(t)\rangle = E_n(t)\,|n(t)\rangle \tag{4.17}$$

The state vector is then expressed in terms of the instantaneous solutions

$$|\psi\rangle = \sum_n a_n(t)\,|n(t)\rangle \exp\left[\frac{i}{\hbar}\int_o^t E_n(t')dt'\right] \tag{4.18}$$

where a_n are time dependent coefficients. The state vector satisfies the time dependent Schrodinger equation

$$i\hbar\,\frac{\partial|\psi\rangle}{\partial t} = \hat{H}(t)\,|\psi\rangle \tag{4.19}$$

For ease of notation, the explicit time dependence of the various terms will be dropped. Substituting Eq (4.18) into (4.19) and simplifying,

$$\sum_n \dot{a}_n|n\rangle \exp\left[\frac{1}{i\hbar}\int_o^t E_n dt'\right] = -\sum_n a_n|\dot{n}\rangle \exp\left[\frac{1}{i\hbar}\int_o^t E_n dt'\right] \tag{4.20}$$

Multiplying both sides by $\langle k|$

$$\dot{a}_k = -\sum_n a_n \langle k|\dot{n}\rangle \exp\left[\frac{1}{i\hbar}\int_o^t (E_n - E_k)\,dt'\right] \tag{4.21}$$

This is an expression for the time rate of change of the expansion coefficients. An expression for $\langle k|\dot{n}\rangle$ comes from differentiating Eq (4.17) and multiplying by $\langle k|$

$$\langle k|\frac{\partial \hat{H}}{\partial t}|\, n\rangle + \langle k|\hat{H}|\dot{n}\rangle = \langle k|\frac{\partial E_n}{\partial t}|\, n\rangle + \langle k|E_n|\dot{n}\rangle \tag{4.22}$$

For $k \neq n$,

$$\langle k|\frac{\partial E_n}{\partial t}|\, n\rangle = \frac{\partial E_n}{\partial t}\langle k|n\rangle = 0 \tag{4.23}$$

$$\langle k|\hat{H}|\dot{n}\rangle = \langle k|E_k|\dot{n}\rangle \tag{4.24}$$

Thus, Eq (4.22) becomes

$$\langle k|\dot{n}\rangle = \frac{\langle k|\frac{\partial \hat{H}}{\partial t}|n\rangle}{E_n - E_k} \qquad n \neq k \tag{4.25}$$

For the case of $k = n$, it is possible to put a condition on the phase of the eigenstates, such that $\langle n|\dot{n}\rangle = 0$ (6:290). The final relation for the coefficients is

$$\dot{a}_k = -\sum_{n\neq k} \frac{a_n}{\hbar\omega_{nk}} \langle k|\frac{\partial H}{\partial t}|n\rangle \exp\left[i\int_o^t \omega_{nk}\, dt'\right] \tag{4.26}$$

where

$$\omega_{nk}(t) = \frac{E_n(t) - E_k(t)}{\hbar} \tag{4.27}$$

This relation describes transitions between the time dependent energy eigenstates.

The form of Eq (4.26) is considerably different than its counterparts for the first two Hamiltonians, Eqs (2.19) and (2.31). The transition matrix depends on $\partial\hat{H}/\partial t$, which is $-e\bar{r}\cdot\partial\bar{E}/\partial t$ in the electric dipole form. The exponential term contains an integral, since the transition frequency is time dependent. Finally, recall that the eigenstates are functions of time, as well. In the previous case of the full Hamiltonian, Eq (2.30), the eigenstates are functions of time, but are unitarily related to the unperturbed eigenstates, simplifying the solution. Unfortunately, this is not the case for Eq (4.26). These differences translate to a significantly more difficult solution when applying Eq (4.26) to a particular experimental setup.

Physical predictions using the multipole form for the energy operator should differ from those of the unperturbed or full atomic Hamiltonian. The choice of the energy operator is most important in describing such phenomenon as multiphoton processes, atomic lineshapes, non-exponential decay rates, and absorption sidebands. The difference in predictions of the three models is a means of confirming the correct choice for the energy operator. Already, a possi-

bility exists in the Stark effect for a transverse electric field. The multipole Hamiltonian is the only one that has an equal dependence on the longitudinal and transverse electric fields. Measuring a Stark shift for a transverse field should distinguish between the various Hamiltonians. This is not a trivial task, since very strong fields are required. Another possibility is in the explanation of the absorption sidebands for OCS in a time varying electric field, observed by Townes et.al.(21:273-279; 22). Townes uses a perturbation calculation, but the multipole Hamiltonian may yield a better explanation. This is an area for further study.

In any case, the multipole Hamiltonian is a plausible choice for the energy operator, and could be used to explain many physical phenomena. In the next chapter, a multiphoton process is examined to show the different predictions of the three energy operators, and provide a means of experimental confirmation.

V. Three Photon Absorption Calculations

The ultimate confirmation of the multipole form of the Hamiltonian as the energy operator depends on correlation with experimental results. Comparison between the predictions of Eq (4.26) and those of the other two choices, Eqs (2.20) and (2.31), should indicate the proper choice. One physical process which has a significant difference between predictions is three photon absorption. This last chapter details the calculations for three photon absorption of the three Hamiltonians. Order of magnitude differences exist, as well as a difference in the resonant frequencies.

To simplify the calculations, a two level system is assumed. This is a reasonable assumption, since many atomic systems can be approximated in this way or forced into such a condition. In addition, spontaneous emission is ignored in the calculations, which allows much simplification of the rate equations. If the experimental evaluation is made on a time scale short compared to the spontaneous emission rate, the assumption is valid.

Calculations for $\hat{H}$ and $\hat{H}_o$

The Schrodinger equation for the full atomic Hamiltonian, $\hat{H}$, can be expressed in the form of Eq (2.31),

$$\dot{a}_n = \frac{1}{i\hbar} \sum_m \langle \varepsilon_n | -e\hat{\bar{r}} \cdot \bar{E} | \varepsilon_m \rangle a_m e^{i\omega_{nm} t} \qquad (5.1)$$

where the coefficients a_n represent the expansion coefficients of the true energy eigenstates. The eigenstates in the transition matrix are those of the unperturbed Hamiltonian,

$$\hat{H}_o|\varepsilon_n\rangle = \varepsilon_n|\varepsilon_n\rangle \tag{5.2}$$

If the atom is assumed initially to be in the ground state of a two level system, then the time evolution of a_2 describes the absorption rate for a given electric field. The solution of Eq (5.1) involves the use of time dependent perturbation theory. For three photon absorption, third order perturbation terms are required.

For a two level system, Eq (5.1) becomes a pair of coupled rate equations:

$$\dot{a}_1 = \frac{1}{i\hbar}\langle\varepsilon_1|-e\hat{\bar{r}}\cdot\bar{E}|\varepsilon_2\rangle a_2 e^{-i\omega_o t} \tag{5.3a}$$

$$\dot{a}_2 = \frac{1}{i\hbar}\langle\varepsilon_2|-e\hat{\bar{r}}\cdot\bar{E}|\varepsilon_1\rangle a_1 e^{+i\omega_o t} \tag{5.3b}$$

where the transition frequency is defined as

$$\omega_o = \frac{\varepsilon_2 - \varepsilon_1}{h} \tag{5.4}$$

and $\hat{H}' = -e\hat{\bar{r}}\cdot\bar{E}$ is the perturbation. Let the electric field be linearly polarized, and defined as $\bar{E} = \xi \cos\omega t\ \hat{n}$, where $\hat{n}$ is the orientation unit vector. Also define

$$\mu = e\langle\varepsilon_1|\hat{\bar{r}}|\varepsilon_2\rangle\cdot\hat{n} \tag{5.5}$$

The transition matrix for this two level system is

$$H'_{nm} = \begin{bmatrix} o & -\xi\mu\cos\omega t \\ -\xi\mu\cos\omega t & o \end{bmatrix} \tag{5.6}$$

Eqs (5.3) then become

$$\dot{a}_1 = i\Omega a_2 \cos\omega t\ e^{-i\omega_o t} \tag{5.7a}$$

$$\dot{a}_2 = i\Omega a_1 \cos\omega t\ e^{i\omega_o t} \tag{5.7b}$$

where $\Omega = \frac{\mu\xi}{\hbar}$, is the Rabi frequency.

From time dependent perturbation theory, let

$$\hat{H}' = -\lambda e\hat{\bar{r}}\cdot\bar{E} \tag{5.8}$$

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \ldots \tag{5.9}$$

Substituting into Eq (5.1) and equating powers of λ ,

$$a_k^{(m)} = \frac{1}{i\hbar}\sum_n \int_o^t a_n^{(m-1)} \langle k|\hat{H}'|n\rangle e^{i\omega_{nk}t'}dt' \tag{5.10}$$

This equation expresses the mth order perturbation in terms of the previous one. Eqs (5.7) then become

$$\dot{a}_1^{(m)} = i\Omega\int_o^t a_2^{(m-1)} \cos\omega t \; e^{-i\omega_o t} \, dt \tag{5.11a}$$

$$a_2^{(m)} = i\Omega\int_o^t a_1^{(m-1)} \cos\omega t \; e^{+i\omega_o t} \, dt \tag{5.11b}$$

If the two level system is initially in the ground state, $a_n^{(0)}(t) = a_n(0) = \delta_{n1}$. The first order perturbation is $a_1^{(1)} = 0$, and

$$a_2^{(1)} = i\Omega\int_o^t \cos\omega t \; e^{i\omega_o t} dt$$

$$= \frac{\Omega}{2}\left[\frac{e^{-i(\omega_o+\omega)t}-1}{\omega_o+\omega} + \frac{e^{i(\omega_o-\omega)t}-1}{\omega_o-\omega}\right] \tag{5.12}$$

This is the familiar first order perturbation calculation, which describes resonant single photon absorption. When ω approaches the transition frequency, ω_o , the second term becomes relatively large, and a_2 takes the form of a sinc function. The sinc function has a series of sidelobes which are unphysical. This results from the unnatural assumption of an instantaneous switching on of the electric field, and is not physically significant.

The second order perturbation is

$$a_1^{(2)} = i\Omega\int_o^t a_2^{(1)} \cos\omega t \; e^{-i\omega_o t} \, dt \tag{5.13}$$

$$a_1^{(2)} = \frac{\Omega^2}{4}\left[\frac{e^{2i\omega t}-1}{2\omega(\omega_o+\omega)} + \frac{t}{\omega_o+\omega}\right.$$

$$+ \frac{2\omega_o}{\omega_o^2-\omega^2}\left(\frac{e^{-i(\omega_o-\omega)t}-1}{\omega_o-\omega} + \frac{e^{-i(\omega_o+\omega)t}-1}{\omega_o+\omega}\right)$$

$$\left. + \frac{t}{\omega_o-\omega} - \frac{e^{-2i\omega t}-1}{2\omega(\omega_o-\omega)}\right] \qquad (5.14)$$

The third order perturbation uses Eq (5.14)

$$a_2^{(3)} = i\Omega\int_o^t a_1^{(2)}\cos\omega t\, e^{i\omega_o t}\, dt \qquad (5.15)$$

Expanding the integrand,

$$a_2^{(3)} = i\left(\frac{\Omega}{2}\right)^3\int_o^t\left[\frac{e^{i(\omega_o+3\omega)t}}{2\omega(\omega_o+\omega)} - \frac{e^{i(\omega_o-\omega)t}}{2\omega(\omega_o+\omega)}\right.$$

$$+ \frac{2\omega_o t}{\omega_o^2-\omega^2}\left(e^{i(\omega_o+\omega)t} + e^{i(\omega_o-\omega)t}\right)$$

$$+ \frac{2\omega_o}{\omega_o^2-\omega^2}\left(\frac{e^{2i\omega t}}{\omega_o-\omega} + \frac{1}{\omega_o+\omega} + \frac{1}{\omega_o-\omega} + \frac{e^{-2i\omega t}}{\omega_o+\omega}\right)$$

$$\left. + \frac{e^{i(\omega_o+\omega)t}}{2\omega(\omega_o-\omega)} - \frac{e^{i(\omega_o-3\omega)t}}{2\omega(\omega_o-\omega)}\right] dt \qquad (5.16)$$

This equation finally yields the three photon absorption term. When $\omega \simeq \omega_o/3$, the last term becomes slowly varying, and thus increases greatly after integration. It is the only physically significant term, although other terms of the form $1/\omega_o \pm \omega$ are also slowly varying. These additional terms are essentially constant over the range of interest, $\omega_o/3$; thus, it is felt they are unphysical and a result of a limitation in the perturbation approach. Further justification for ignoring these terms is given when the final solution is compared to an exact solution of this problem. Dropping the unnecessary terms,

$$a_2^{(3)} \simeq - i \left(\frac{\Omega}{2}\right)^3 \int_o^t \frac{e^{i(\omega_o - 3\omega)t}}{2\omega(\omega_o - \omega)} dt$$

$$= \left(\frac{\Omega}{2}\right)^3 \frac{1 - e^{i(\omega_o - 3\omega)t}}{2\omega(\omega_o - \omega)(\omega_o - 3\omega)} \qquad (5.17)$$

For three photon absorption, $\omega \simeq \omega_o/3$, there are no contributing factors from the first order perturbation, Eq (5.12). The upper level coefficient is then $a_2 = a_2^{(3)}$. The probability of being in the upper energy state is

$$P_2(t) = |a_2(t)|^2 \qquad (5.18)$$

which can be written as

$$P_2(t) = \frac{81}{256} \frac{\Omega^6}{\omega_o^4} \frac{\sin^2 \frac{1}{2}(\omega_o - 3\omega)t}{(\omega_o - 3\omega)^2} \tag{5.19}$$

This equation represents the probability for three photon absorption for the full atomic Hamiltonian. The resonant frequency is $\omega = \omega_o/3$.

As a comparison, the exact solution from Shirley (23:983-985) is

$$P_2(t) = \frac{81}{256} \frac{\Omega^6}{\omega_o^4} \frac{\sin^2 \frac{1}{2}\left[\frac{\Omega^4}{4\omega_o^4} + (3\omega - \omega_o)^2\right]^{\frac{1}{2}} t}{\frac{\Omega^4}{4\omega_o^4} + (3\omega - \omega_o)^2} \tag{5.20}$$

The two equations are very close for small t. When $(3\omega - \omega_o)^2 >> \Omega^4/4\omega_o^4$, the equations are the same, and as ω approaches $\omega_o/3\omega$, they have the same limit. If t is large, the perturbation method is not valid, since the perturbation is assumed to be small. The favorable comparison gives further justification for ignoring the extra terms of Eq (5.16). The results from the perturbation calculation are also comparable to the method of Autler and Townes (22).

Treating the unperturbed Hamiltonian as the energy operator results in a perturbation of the form $\hat{H}' = -e/mc\, \bar{A} \cdot \hat{\bar{p}}$, and after Eq (2.19), the Schrodinger equation becomes

$$\dot{a}_n = \frac{1}{i\hbar} \sum_m \langle n | -\frac{e}{mc} \bar{A} \cdot \hat{\bar{p}} | \varepsilon_m \rangle a_m e^{i\omega_{nm} t} \tag{5.21}$$

The only difference between Eq (5.21) and Eq (5.1) is the transition matrix. Kobe (13:626) shows that the matrix elements are related such that

$$\langle \varepsilon_n | \frac{e}{mc} \bar{A} \cdot \hat{\bar{p}} | \varepsilon_m \rangle = \frac{\omega_{nm}}{\omega} \langle \varepsilon_n | e\hat{\bar{r}} \cdot \bar{E} | \varepsilon_m \rangle \tag{5.22}$$

Thus, the development ior the unperturbed Hamiltonian parallels the previous calculation except for a constant. Each perturbation term changes by a factor of ω_o/ω . For a third order perturbation, the expansion coefficient is multiplied by $(\omega_o/\omega)^3$. The probability of being in the upper energy state is now

$$P_{2_{A\cdot p}}(t) = \left(\frac{\omega_o}{\omega}\right)^6 P_2(t) \tag{5.23}$$

Thus, for $\hat{H}_o$, the probability for three photon absorption is

$$P_{2_{A\cdot p}}(t) = 9^3 \frac{81}{256} \frac{\Omega^6}{\omega_o^4} \frac{\sin^2 \frac{1}{2}(\omega_o - 3\omega)t}{(\omega_o - 3\omega)^2} \tag{5.24}$$

The result is about three orders of magntiude greater than that of the full Hamiltonian.

Multipole Hamiltonian Calculation

The final calculation is for the multipole Hamiltonian, which presents some distinct differences, primarily due to the time dependence of the energy eigenstates and eigenvalues.

The general method of solution is to solve for the instantaneous eigenstates and eigenvalues of Eq (4.17), treating t as a constant parameter. The instantaneous solutions can then be used in Eq (4.26), which can then be solved using time dependent perturbation theory.

For a two level system, Eq (4.26) becomes a pair of coupled rate equations

$$\dot{a}_1 = -\frac{a_2}{\hbar\omega_{21}} \langle 1| \frac{\partial \hat{H}}{\partial t} |2\rangle \, e^{-i\int_o^t \omega_{21} dt'} \tag{5.25a}$$

$$\dot{a}_2 = \frac{a_1}{\hbar\omega_{21}} \langle 2| \frac{\partial \hat{H}}{\partial t} |1\rangle \, e^{i\int_o^t \omega_{21} dt'} \tag{5.25b}$$

Solution of these equations is not trivial due to the time dependence of the eigenstates and eigenvalues. The energy eigenstates, $|n\rangle$, are the instantaneous solutions of the time independent Schrodinger equation

$$\hat{H}(t)|n(t)\rangle = E_n(t)|n(t)\rangle \tag{5.26}$$

The solution follows the method of Cohen-Tannoudji (1:406-408), 420-423). The multipole Hamiltonian can be written as

$$\hat{H}(t) = \hat{H}_o - e\hat{\bar{r}}.\bar{E}(t) \tag{5.27}$$

Using the unperturbed eigenstates $|\varepsilon_n\rangle$ as the representation basis set, $\hat{H}$ can be expressed in matrix form:

$$H_{nm} = \langle\varepsilon_n|\hat{H}|\varepsilon_m\rangle = \begin{bmatrix} \varepsilon_1 & -\mu\xi\cos\omega t \\ -\mu\xi\cos\omega t & \varepsilon_2 \end{bmatrix} \tag{5.28}$$

where μ is defined by Eq (5.5). Diagonalizing H_{nm} determines the true energy eigenvalues,

$$E_1 = \frac{1}{2}(\varepsilon_1+\varepsilon_2) - \frac{\hbar}{2}\left[\omega_o^2+\Omega^2\cos^2\omega t\right]^{\frac{1}{2}} \tag{5.29a}$$

$$E_2 = \frac{1}{2}(\varepsilon_1+\varepsilon_2) + \frac{\hbar}{2}\left[\omega_o^2+\Omega^2\cos^2\omega t\right]^{\frac{1}{2}} \tag{5.29b}$$

where again

$$\omega_o = \frac{\varepsilon_2-\varepsilon_1}{\hbar} \qquad \Omega = \frac{\mu\xi}{\hbar}$$

The instantaneous transition frequency is

$$\omega'(t) = \frac{\varepsilon_2-\varepsilon_1}{\hbar} = \left[\omega_o^2+\Omega^2\cos^2\omega t\right]^{\frac{1}{2}} \tag{5.30}$$

which oscillates in time, above the unperturbed value. The oscillation may be the primary cause for such phenomenon as multiphoton absorption and absorption sidebands. The eigenstates, in the ε_n representation are

$$|1\rangle = \begin{pmatrix} \cos\theta \\ -\sin\theta \end{pmatrix} \qquad |2\rangle = \begin{pmatrix} \sin\theta \\ \cos\theta \end{pmatrix} \tag{5.31}$$

where

$$\tan 2\theta = -\frac{\Omega}{\omega_o}\cos\omega t \tag{5.32}$$

The transition matrix of Eq (5.25) can now be determined using Eqs (5.5) and (5.31):

$$\frac{\partial \hat{H}}{\partial t} = -\, e\hat{\bar{r}}\cdot\frac{\partial \bar{E}}{\partial t} \tag{5.33}$$

$$\langle 1|\frac{\partial \hat{H}}{\partial t}|2\rangle = \hbar\omega\Omega\, \cos 2\theta\, \sin\omega t = \langle 2|\frac{\partial H}{\partial t}|1\rangle \tag{5.34}$$

From Eq (5.11),

$$\cos 2\theta = \frac{\omega_o}{\left[\omega_o^{\,2}+\Omega^2\cos^2\omega t\right]^{\frac{1}{2}}} = \frac{\omega_o}{\omega'} \tag{5.35}$$

Thus, Eqs (5.25) become

$$\dot{a}_1 = -a_2\,\frac{\omega_o\omega\Omega}{\omega'^2}\,\sin\omega t\; e^{-i\int_o^t \omega' dt'} \tag{5.36a}$$

$$\dot{a}_2 = a_1\,\frac{\omega_o\omega\Omega}{\omega'^2}\,\sin\omega t\; e^{i\int_o^t \omega' dt'} \tag{5.36b}$$

These are exact equations, but approximations must be used to arrive at manageable solutions.

From time dependent perturbation theory, let

$$\frac{\partial \hat{H}}{\partial t} = - \lambda e \hat{\bar{r}} \cdot \frac{\partial \bar{E}}{\partial t} \tag{5.37}$$

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \ldots \tag{5.38}$$

Substituting into Eq (4.26) and equating equal powers of λ

$$a_k^{(m)} = - \sum_{n \neq k} \int_o^t a_n^{(m-1)} \frac{\langle k | \frac{\partial \hat{H}}{\partial t} | n \rangle}{h\omega_{nk}} e^{-i\int_o^t \omega_{nk} dt'} \tag{5.39}$$

This equation is comparable to Eq (5.10).

If the two level system is initially in the ground state, the first order perturbation for the upper energy level is

$$a_2^{(1)}(t) = \int_o^t \frac{\omega \omega_o \Omega}{\omega'^2} \sin\omega t \, e^{i\int_o^t \omega' dt'}$$

$$\omega' = \left[\omega_o^2 + \Omega^2 \cos^2 \omega t \right]^{\frac{1}{2}} \tag{5.40}$$

The instantaneous transition frequency ω' can be expanded

$$\omega' \simeq \omega_o + \frac{\Omega^2}{2\omega_o} \cos^2 \omega t + \ldots \tag{5.41}$$

Higher order terms can be ignored provided $\Omega^4 / 4\omega_o^4 << 1$.

The integral in the exponential becomes

$$\int_0^t \omega' dt' = \omega_o t + \frac{\Omega^2}{4\omega_o} t + \frac{\Omega^2}{8\omega_o\omega} \sin\omega t$$

$$= \omega_o' t + \frac{\Omega^2}{8\omega_o\omega}\sin\omega t \qquad (5.42)$$

where $\omega_o' = \omega_o + \Omega^2/4\omega_o$ is the shifted transition frequency, as will be shown later. This shift is a function of the field strength, ξ, which demonstrates the Stark effect for a transverse field. The exponential can be expanded as a series of Bessel functions (24:361):

$$e^{\pm iz\sin\theta} = \sum_{n=-\infty}^{\infty} J_n(z) e^{in\theta} \qquad (5.43)$$

For $z << 1$ (24:358),

$$J_n(z) \simeq \frac{\left(\frac{1}{2}z\right)^n}{\Gamma(n+1)} \qquad (5.44)$$

Using $J_n = (-1)^n J_n$ and $\Gamma(1) = \Gamma(2) = 1$,

$$e^{i\frac{\Omega^2}{8\omega_o\omega}\sin\omega t} \simeq 1 + \frac{\Omega^2}{8\omega_o\omega} i \sin 2\omega t$$

$$+ \left(\frac{\Omega^2}{16\omega_o\omega}\right)^2 \frac{2\cos 4\omega t}{\Gamma(3)} + \ldots \qquad (5.45)$$

Ignoring the higher order terms, the exponential becomes

$$e^{i\int_0^t \omega' dt'} \simeq e^{i\omega_o' t}\left(1 + \frac{\Omega^2}{8\omega_o\omega}\, i\, \sin 2\omega t\right) \qquad (5.46)$$

Expanding the demoninator of Eq (5.40),

$$\frac{1}{\omega'^2} = \frac{1}{\omega_o'^2\left(1+\frac{\Omega^2}{\omega_o^2}\cos^2\omega t\right)}$$

$$\simeq \frac{1}{\omega_o^2}\left[1 - \frac{\Omega^2}{\omega_o^2}\cos^2\omega t + \frac{\Omega^4}{\omega^4}\cos^4\omega t + \ldots\right] \qquad (5.47)$$

Finally, Eq (5.40) becomes

$$a_2^{(1)} \simeq \int_o^t \frac{\omega\Omega}{\omega_o}\left(1 - \frac{\Omega^2}{\omega_o^2}\cos^2\omega t\right)\sin\omega t$$

$$x\left(1 + \frac{\Omega^2}{8\omega_o\omega}\, i\, \sin 2\omega t\right) e^{i\omega_o' t}\, dt \qquad (5.48)$$

which is directly integrable, although messy. Expanding the integrand and dropping terms of higher order than Ω^3 ,

$$a_2^{(1)} = \frac{\omega\Omega}{2\omega_o i} \int_o^t \left[\left(1 - \frac{\Omega^2}{4\omega_o^2} - \frac{\Omega^2}{16\omega_o\omega} \right) e^{i(\omega_o' + \omega)t} \right.$$

$$- \left(1 - \frac{\Omega^2}{4\omega_o^2} + \frac{\Omega^2}{16\omega_o\omega} \right) e^{i(\omega_o' - \omega)t}$$

$$+ \left(\frac{\Omega^2}{16\omega_o\omega} - \frac{\Omega^2}{4\omega_o^2} \right) e^{i(\omega_o' + 3\omega)t}$$

$$\left. + \left(\frac{\Omega^2}{16\omega_o\omega} + \frac{\Omega^2}{4\omega_o^2} \right) e^{i(\omega_o' - 3\omega)t} \right] dt \qquad (5.49)$$

Notice that only odd harmonics of ω are present in the exponential terms. Absorption occurs only when a term becomes slowly varying, when the exponential argument approaches zero. Therefore, only an odd number of photons can be absorbed, in this model. The conclusion corresponds to the conservation of angular momentum. The angular momentum must change by one unit in the transition, and photons have one unit of angular momentum. Only odd combinations are possible.

Integrating Eq (5.49)

$$a_2^{(1)} = -\frac{\omega\Omega}{2\omega_o}\left[\left(1 - \frac{\Omega^2}{4\omega_o^2} - \frac{\Omega^2}{16\omega_o\omega}\right)\frac{e^{i(\omega_o'+\omega)t}-1}{\omega_o'+\omega}\right.$$

$$- \left(1 - \frac{\Omega^2}{4\omega_o^2} + \frac{\Omega^2}{16\omega_o\omega}\right)\frac{e^{i(\omega_o'-\omega)t}-1}{\omega_o'-\omega}$$

$$+ \left(\frac{\Omega^2}{16\omega_o\omega} - \frac{\Omega^2}{4\omega_o^2}\right)\frac{e^{i(\omega_o'+3\omega)t}-1}{\omega_o'+3\omega}$$

$$\left. + \left(\frac{\Omega^2}{16\omega_o\omega} + \frac{\Omega^2}{4\omega_o^2}\right)\frac{e^{i(\omega_o'-3\omega)t}-1}{\omega_o'-3\omega}\right] \qquad (5.50)$$

$a_2^{(1)}$ gets relatively large whenever ω approaches ω_o', the shifted transition frequency, or $\omega_o'/3$, three photon absorption. If $\omega \simeq \omega_o'/3$, then only the last term is of importance, and since $\omega_o' \simeq \omega_o$,

$$a_2^{(1)} \simeq -i\,\frac{7}{48}\,\frac{\Omega^3}{\omega_o^2}\,\frac{\sin\frac{1}{2}(\omega_o'-3\omega)t}{\omega_o'-3\omega}\,e^{\frac{i}{2}(\omega_o'-3\omega)t} \qquad (5.51)$$

It is necessary to calculate higher order perturbation terms since they contribute terms of order Ω^3. Recall that since the atom is initially in the ground state, the perturbation terms $a_1^{(1)} = a_2^{(2)} = 0$. But,

$$a_1^{(2)} = -\int_o^t a_2^{(1)} \frac{\omega_o \omega \Omega}{\omega'^2} \sin\omega t \, e^{-i\int_o^t \omega' dt'} dt \qquad (5.52)$$

which is similar in form to Eq (5.40). Expanding the integrand as before, using Eq (5.50) for $a_2^{(1)}$, and dropping higher order terms of Ω results in an integrable form. The solution of $a_1^{(2)}$ is then used in the calculation of the third order perturbation:

$$a_2^{(3)} = \int_o^t a_1^{(2)} \frac{\omega_o \omega \Omega}{\omega'^2} \sin\omega t \, e^{i\int_o^t \omega' dt'} dt \qquad (5.53)$$

Again, if $\omega \simeq \omega_o'/3$, only one physically significant term in the integrand is slowly varying. Other unphysical terms are also slowly varying, but these can be ignored as in the previous case, Eq (5.16). The perturbation term becomes

$$a_2^{(3)} \simeq -\left(\frac{\omega\Omega}{2\omega_o}\right)^3 \int_o^t \frac{e^{i(\omega_o'-3\omega)t}}{2i\omega(\omega_o'-\omega)} dt \qquad (5.54)$$

The result of the integration can be expressed as

$$a_2^{(3)} \simeq \frac{i}{48} \frac{\Omega^3}{\omega_o^2} \frac{\sin\frac{1}{2}(\omega_o'-3\omega)t}{(\omega_o'-3\omega)} e^{\frac{i}{2}(\omega_o-3\omega)t} \qquad (5.55)$$

The final expression for a_2 is $a_2 = a_2^{(1)} + a_2^{(3)}$, which from Eqs (5.51) and (5.55) is

$$a_2 = -i \frac{\Omega^3}{8\omega_o^2} \frac{\sin\frac{1}{2}(\omega_o'-3\omega)t}{(\omega_o'-3\omega)} e^{\frac{i}{2}(\omega_o'-3\omega)t} \tag{5.56}$$

The probability of being in the upper energy level is

$$P_2(t) = |a_2(t)|^2$$
$$= \frac{\Omega^6}{64\omega_o^4} \frac{\sin^2\frac{1}{2}(\omega_o'-3\omega)t}{(\omega_o'-3\omega)^2} \tag{5.57}$$

which represents the transition for three photon absorption with the multipole Hamiltonian. The resonant frequency for this transition is

$$\omega = \frac{\omega_o'}{3} = \frac{\omega_o}{3} + \frac{\Omega^2}{12\omega_o} \tag{5.58}$$

The results for the multipole Hamiltonian, Eqs (5.57) and (5.58) are much different than those of the other two Hamiltonians.

Comparison of Predictions

Calculations for the three Hamiltonians shows considerable differences in the predictions for the probability of a two level atom, initially in the ground state, to transition to the upper energy level. In each case, time dependent perturbation theory was used to determine the probability. The method is valid for relatively short time periods, otherwise effects such as Rabi oscillations and spontaneous

emission become important. In addition to the transition rate difference, the multipole Hamiltonian case also showed a Stark shift for a transverse electric field. The first two Hamiltonians do not account for such an effect.

The differences in the upper level predictions is most easily seen for radiation that is exactly on resonance, $\omega = \omega_o/3$. The probabilities for the three cases are

$$P_{2Ap}(t) = 9^3 \frac{81}{1024} \frac{\Omega^6}{\omega_o^2} t^2 \tag{5.59}$$

$$P_{2rE}(t) = \frac{81}{1024} \frac{\Omega^6}{\omega_o^2} t^2 \tag{5.60}$$

$$P_{2MH}(t) = \frac{\Omega^6}{256\omega_o^4} t^2 \tag{5.61}$$

Thus,

$$P_{2Ap} \simeq 10^3 P_{2rE} \simeq 2\text{x}10^4 P_{2MH} \tag{5.62}$$

This demonstrates the order of magnitude differences between the three choices. These differences are directly translated to comparable differences in the absolute transition rates or the Einstein B coefficients. The rate for the multipole Hamiltonian is the smallest by a factor of twenty. If the absolute rate could be measured, it would strongly indicate the correct choice for the energy operator.

Absolute transition rates for a three photon process are, unfortunately for this problem, difficult to measure. First, there is a requirement for a very strong field to obtain an appreciable amount of transitions. Assuming a sufficient source is available, there are problems with the media itself. In crystals, the problem of wave vector matching (25:76-78) severely hinders absolute measurements. The problem is non-exponential absorption due to interference effects in the crystal. Another possibility for an experiment is to measure the deflection of an atomic beam by radiation pressure. An incident light wave can cause a beam deflection based on the absorption rate (26). The primary difficulty with this configuration is in generating a stable beam that is slow enough to have a reasonable interaction time.

The other major difference in the predictions was the resonant frequency shift predicted only in the multipole Hamiltonian case. Considering either the unperturbed or the full atomic Hamiltonian as the energy operator allows no shift due to a transverse electric field, although such shifts have been observed for time varying fields (22). The prediction of this Stark shift for the multipole Hamiltonian may be the best argument for this choice as the energy operator.

VI. Conclusion

The choice of the correct form of the Hamiltonian as the energy operator has significant implications for physical predictions in quantum mechanics. Historically, two choices have been predominant: the unperturbed Hamiltonian and the full atomic Hamiltonian. Each results in different predictions as indicated by their respective transition matrices. This difference is often clouded by the equivalence of these two forms under a unitary transformation. The argument for equivalence is valid, based on interpretation of the eigenstates, but it does not address the identification of the atomic energy operator. This thesis has argued that both of these choices are limited due to conflicts with either observed phenomenon or physical laws, and neither represents the true energy of the atom.

Another possibility for the energy operator exists in the multipole expansion form of the Hamiltonian. It is derived from the classical multipole energy expansion, and has the correct classical limit of the Lorentz force law. The multipole form is gauge invariant, and contains the total field, so it does not violate special relativity. The dynamics of this form are much more complicated than the previous cases, which compounds the difficulty of making physical predictions. Thus, for the purposes of first order approximations, the unperturbed or full atomic Hamiltonian should prove to be an

adequate, though not completely accurate, choice for the energy operator. For finer applications, the multipole form may provide the better model for the atom, and hence, a more accurate explanation for physical processes.

Calculations for three photon absorption demonstrate the differences between predictions of the three choices for the energy operator. Order of magnitude differences exist for the probability of transitioning to the upper state of a two level atom. These directly translate to comparable differences in the absolute transition rates. The multipole Hamiltonian has a further distinction of predicting a Stark shift for a transverse electric field. The other two Hamiltonians do not allow this shift in the respective models.

Experimental confirmation of the absorption prediction or the Stark effect due to a transverse field is the final proof of this thesis. Unfortunately, measurement of an absolute three photon absorption rate is a difficult task, and has not been performed. This is an area for further investigation. In addition, Stark shifts have been observed in numerous experiments (22). Further study of those experimental results and the methods of analysis is warranted. The Stark effect may provide the best confirmation of the correct energy operator.

Another suggestion for future work is to consider the affect of spontaneous emission in the absorption calculations. The steady state solution to a density matrix perturbation

calculation should give the absorption rate for long interaction times, and spurious zero frequency terms, previously disregarded, should be damped out.

Other recommendations include the investigation of absorption sidebands, observed by Townes (21:273-279), and atomic lineshapes. These areas may provide further arguments for choosing the multipole Hamiltonian as the atomic energy operator.

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Various forms of the atomic Hamiltonian are examined as the energy operator for an atom in an electromagnetic field, using the semiclassical approach. The unperturbed Hamiltonian and the full atomic Hamiltonian have been favorite choices in the past, but these give different predictions if treated as the energy operator. The $A \cdot p$ versus $r \cdot E$ controversy is also examined and clarified. Both choices have conflicts with observations or physical laws. Gauge invariance and the Stark effect are considered. The multipole Hamiltonian is presented and argued as the correct energy operator. Calculations for three photon absorption in a two level atom, using time dependent perturbation theory, yield significant differences in the predictions for absorption rate and resonant frequency.

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