Electron Magnetic Resonance: The Modified Bloch Equation

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We find a modified Bloch equation for the electronic magnetic moment when the magnetic moment explicitly contains a diamagnetic contribution (a magnetic field induced magnetic moment arising from the electronic orbital angular momentum) in addition to the intrinsic magnetic moment of the electron. The modified Bloch is coupled to equations of motion for the position and momentum operators. In the presence of static and time varying magnetic field components, the magnetic moment oscillates out of phase with the magnetic field and power is absorbed by virtue of the magnetic field induced magnetic moment, even in the absence of coupling to the environment. We explicitly work out the spectrum and absorption for the case of a $p$ state electron.

I. INTRODUCTION

The importance of magnetic resonance methods to chemical analysis, solid-state physics, biological structure determination and medicine is well recognized. In magnetic resonance experiments, a material is placed in dc and oscillating magnetic fields and the power absorption is measured. The power absorption exhibits spectra containing resonances, from which valuable information about the system is obtained.

The Bloch equation describing the dynamics of the magnetic moment operator $\vec{\mu}$ is:

$$\frac{d\vec{\mu}}{dt} = -\frac{\mu_0\gamma}{\hbar}\vec{B} \times \vec{\mu}. \tag{1}$$

Its solution is discussed in textbook theoretical treatments of magnetic resonance [1]. Here, $\mu_0 = \frac{e\hbar}{2m}$ is the Bohr magneton, and $\gamma$ is a dimensionless constant. SI units are employed throughout. This equation has played a major role in understanding magnetic resonance experiments ever since it was first derived by Bloch in 1946 [2]. In the usual treatment, coupling to the surrounding, i.e., to additional degrees of freedom of the system (often described as a thermodynamic bath), is incorporated into the description by adding phenomenological relaxation (decay) terms to the Bloch equation [3–5]. The additional phenomenological decay terms arise when the bath degrees of freedom of the system are adiabatically eliminated from the description. The external magnetic field in magnetic resonance experiments has a temporally-constant strong component, and a weaker oscillating component of radio-frequency or microwave radiation, which in one common configuration is linearly polarized and perpendicular to the dc component:

$$\vec{B} = B_0 \hat{z} + B_1 (e^{i\omega t} + e^{-i\omega t}) \hat{x} ; \quad B_1 \ll B_0 \tag{2}.$$ 

It is a straightforward generalization to treat the case when the magnetic field contains a rotating oscillating field: $\vec{B}_c = B_0 \hat{z} + \sqrt{2}B_1 [\hat{x}\cos(\omega t) - \hat{y}\sin(\omega t)]$. Here we consider linear polarization. For atomic and molecular systems it is an excellent approximation to neglect the spatial dependence of the oscillating field because the wavelength is so much larger than the size of the atom or molecule.

The power absorption $P$ of a magnetic moment $\vec{\mu}$ in the external field $\vec{B}$ is given by:

$$P = \left[-\langle \vec{\mu}\rangle \cdot \frac{d\vec{B}}{dt}\right]_{t} = \left[\vec{B} \cdot \frac{d\langle \vec{\mu}\rangle}{dt}\right]_{t}, \tag{3}$$

where $\langle ... \rangle$ stands for quantum expectation value and $[...]_t$ for time averaging. Power can only be absorbed if $\vec{B}$ and $\vec{\mu}$ oscillate out of phase, and $\vec{\mu}$ has a component along $\frac{d\vec{B}}{dt}$. The Bloch equation without relaxation terms, Eq. (1), results in no power absorption, since clearly, $\vec{B} \cdot (\vec{B} \times \vec{\mu}) = 0$. In this treatment, the phase shift between the oscillations of $\vec{B}$ and $\vec{\mu}$, necessary for power absorption, exists only because of the relaxation terms. Without those, Eq. (1), implies that power absorption is impossible.
This theoretical framework is adequate for the description of both NMR (Nuclear Magnetic Resonance) and ESR (Electron Spin resonance). It is generally not correct for EMR (Electron Magnetic Resonance). The Bloch equation is not the correct equation of motion for the magnetic moment operator of an electron with non-vanishing orbital angular momentum. Orbital angular momentum effects in magnetic resonance phenomena can be important, not just in gases, but even in solids, e.g., the transition and lanthanide ions doped in crystals where quenching (the modification of the magnetic susceptibility to values close to those produced by electron spin alone due to large crystal field splittings) does not occur. Here we show that, due to diamagnetic effects arising from the electronic orbital angular momentum, the Bloch equations are replaced by a set of coupled operator equations for the magnetic moment \( \mu \) (which incorporates a magnetic field induced magnetic moment contribution), the coordinate \( \vec{r} \) and the velocity operator \( \hat{\Pi}/m \), defined below. The interaction Hamiltonian has non-linear terms arising from a magnetic field induced magnetic moment. As a result, the magnetic moment has an oscillatory component along \( \vec{B} \) and oscillates out of phase with the external field. Hence, power absorption does not vanish, even when coupling to the environment is not included.

In Sec. II we define the magnetic moment operator, including the magnetic field induced magnetic moment contribution, and in Sec. III we derive the Heisenberg equations of motion for a magnetic moment \( \mu \) in the magnetic field \( \vec{B} \). Three coupled equations are obtained in this way, Eqs. (11), (12), and (13) below. Based on these equations, Sec. IV develops general considerations of power absorption in EMR experiments. Since, unlike the Bloch equation, these coupled equations can not be solved in closed form, we solve them in time-dependent perturbation theory, and calculate the power absorption using this analysis. In Sec. V we focus on the example of an electron bound in a p-atomic-orbital, and derive Eq. (13) for the power absorption to leading order in the fields for this case. Section VI presents a summary and conclusion.

II. THE HAMILTONIAN AND THE MAGNETIC MOMENT OPERATOR

The Hamiltonian for an electron, with charge \( q = -e \) and mass \( m \) in a spherically symmetric potential \( \hat{V}(r) \) and an external magnetic field \( \vec{B}(t) \), can be written in terms of the kinetic velocity operator \( \hat{\Pi}/m \) [7]:

\[
\hat{H} = \hat{V}(r) + \frac{\hat{\Pi}^2}{2m}, \tag{4}
\]

\[
\hat{\Pi} \equiv \hat{p} - q\hat{A}, \tag{5}
\]

\[
\hat{A} \equiv \frac{1}{2} \vec{B} \times \hat{r}. \tag{6}
\]

For simplicity, we have neglected the electron spin (which can be re-introduced rather easily as shown in Sec. VII) and chosen a symmetric gauge. The coordinate operator \( \hat{r} \), the conjugate momentum operator \( \hat{p} \), and the velocity operator \( \hat{\Pi}/m \), satisfy the commutation relations: \([r_i,p_j] = [r_i,\Pi_j] = ih\delta_{ij}\), and \([\Pi_i,\Pi_j] = ihq\epsilon_{ijk}B_k\), where \( \epsilon_{ijk} \) is the anti-symmetric Levi-Chivita tensor.

The gauge-invariant operator for the orbital magnetic dipole moment of the electron is given by

\[
\hat{\mu} = \frac{q}{2m} \hat{r} \times \hat{\Pi}. \tag{7}
\]

The magnetic moment operator defined in Eq. (7) is gauge invariant. This can be seen by considering the gauge transformation matrix \( U = \exp[i\hat{\Pi}/\hbar \chi] \) in terms of the gauge function \( \chi(\vec{r},t) \). Under the gauge transformation, the vector potential and the magnetic moment are transformed as follows: \( \vec{A} \to \vec{A}' = \vec{A} + \nabla \chi \), and \( \hat{\mu} \to \hat{\mu}' = U[\frac{q}{2m} \hat{r} \times (\hat{\mu} - q\hat{A})]U^\dagger = \hat{\mu} \).

The Hamiltonian of Eq. (7) can be written in terms of the magnetic moment in the following form:

\[
\hat{H} = \hat{V}(r) + \frac{\hat{p}^2}{2m} - \hat{\mu} \cdot \vec{B} + \frac{q^2}{8m} \left((\vec{B} \cdot \hat{r})^2 - B^2\hat{r}^2\right). \tag{8}
\]

Neglecting all terms of order \( B^2 \) gives: \( \hat{H}' = \hat{V}(r) + \frac{\hat{p}^2}{2m} - \hat{\mu}' \cdot \vec{B} \) and \( \hat{\mu}' \equiv \frac{q}{2m} \hat{r} \times \hat{\mu} \), as used in standard textbook treatments of magnetic resonance. Here, we consider the effect of not neglecting these second order terms, i.e., using \( \hat{H} \) (not \( \hat{H}' \)) with the full \( \hat{\mu} \) (not \( \hat{\mu}' \)).
III. HEISENBERG EQUATIONS

The magnetic moment \( \hat{\mu} \) satisfies the Heisenberg equation of motion: \( \frac{d\hat{\mu}}{dt} = \frac{\partial \hat{\mu}}{\partial t} + \frac{i}{\hbar} \left[ \hat{H}, \hat{\mu} \right] \). Straight-forward algebra gives,

\[
\frac{\partial \hat{\mu}}{\partial t} = \frac{q}{2m} \hat{r} \times \frac{\partial}{\partial t} \hat{\Pi} - \frac{q^2}{4m} \hat{r} \times \left( \frac{\partial}{\partial t} \hat{B} \times \hat{r} \right) = \frac{q^2}{4m} \left( \hat{r} \cdot \frac{\partial}{\partial t} \hat{B} \right) \hat{r} - \hat{r} \times \frac{\partial}{\partial t} \hat{\Pi},
\]

(9)

and, collecting terms, we get:

\[
\frac{d\hat{\mu}}{dt} = \frac{q^2}{4m} \left( \hat{r} \cdot \frac{\partial}{\partial t} \hat{B} \right) \hat{r} - \hat{r} \times \frac{\partial}{\partial t} \hat{\Pi} + \frac{q^2}{2m^2c^2} \left( \hat{r} \times (\hat{B} \times \hat{\Pi}) - i\hbar \hat{B} \right),
\]

(10)

and, collecting terms, we get:

\[
\frac{d\hat{\mu}}{dt} = \frac{q^2}{4m} \left( \hat{r} \cdot \frac{\partial}{\partial t} \hat{B} \right) \hat{r} - \hat{r} \times \frac{\partial}{\partial t} \hat{\Pi} + \frac{q^2}{2m^2c^2} \left( \hat{r} \times (\hat{B} \times \hat{\Pi}) - i\hbar \hat{B} \right).
\]

(11)

The right hand side of Eq. (11) is not equal to \( \frac{\hbar}{m} \hat{B} \times \hat{\mu} \equiv \frac{q^2}{2m^2} \left( \hat{B} \times (\hat{r} \times \hat{\Pi}) \right) \). The Bloch equations are replaced by operator equations whose consistent solution must treat the Heisenberg equation of motions for \( \hat{\mu}(t) \) as well as \( \hat{r}(t) \) and \( \hat{\Pi}(t) \):

\[
\frac{d\hat{r}}{dt} = \hat{\Pi}/m,
\]

(12)

\[
\frac{d\hat{\Pi}}{dt} = \frac{\partial}{\partial t} \hat{\Pi} - \frac{i}{\hbar} \left[ \hat{\Pi}, V(\hat{r}) \right] - \frac{i}{\hbar} \left[ \hat{\Pi}, \hat{\mu}^2/2m \right].
\]

(13)

From these equations we see that energy can be absorbed by the system even under conditions of negligible or no coupling to the environment since \( df/\mu dt \) is no longer perpendicular to \( \hat{B} \). This power absorption in magnetic resonance systems containing electronic orbital angular momentum can also be interpreted as being due to the rate of change of the electric dipole moment in the presence of an electric field. This is evident from the relation:

\[
\frac{\partial \hat{H}}{\partial t} = \frac{e}{2m} \left( \frac{d\hat{B}}{dt} \times \hat{r} \right) \cdot \hat{\Pi} = -\hat{r} \cdot \frac{d\hat{B}}{dt} = \hat{E} \cdot \frac{d\hat{\mu}_E}{dt}.
\]

(14)

Here the electron electric dipole moment is \( \hat{\mu}_E = q\hat{r} = -e\hat{r} \), its time derivative is \( d\hat{\mu}_E/dt = -e\hat{r} \), and the electric field is given by \( \hat{E} = -\partial \hat{A}/\partial t \). Clearly, additional power absorption may result due to coupling to a bath.

The time derivative of the magnetic dipole moment in Eq. (11) can not be written simply in terms of the cross product of the external field and the dipole moment, hence a closed-form analytic solution of the operator equations in the Heisenberg representation is not available. Instead a perturbative solution can be used, as described below.

IV. POWER ABSORPTION

Substituting the magnetic field of Eq. (2) into the Hamiltonian in Eq. (3), we find that the Hamiltonian can be separated into a sum of time-independent and time-dependent parts:

\[
\hat{H} = \hat{H}_0 + \hat{H}_1(t),
\]

(15)

\[
\hat{H}_0 = \hat{V}(\hat{r}) + \frac{\hat{p}^2}{2m} - B_0 \frac{q}{2m} (\hat{z}\hat{p}_y - \hat{y}\hat{p}_z) + B_0 \frac{q^2}{8m} (x^2 + y^2),
\]

(16)

\[
\hat{H}_1(t) = -B_1 (e^{i\omega t} + e^{-i\omega t}) \hat{h}_1; \quad \hat{h}_1 \equiv \frac{q}{2m} (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) + \frac{q^2}{4m} B_0 zx,
\]

(17)
where a term $\hat{H}_2(t)$ of order $B_1^2$ has been neglected. Realistic magnetic fields strengths impose a hierarchy between these terms because usually $|B_0| \gg |B_1|$. For comparison, two frequently used Hamiltonians which give the regular Bloch equation, Eq. (1), are: $\hat{H}^B = \hat{H}_0^B + \hat{H}_1^B(t)$, with:

\begin{align}
\hat{H}_0^B &= \hat{H}_0' = \hat{V}(r) + \frac{\hat{p}^2}{2m} - B_0\hat{\mu}_z, \\
\hat{H}_1^B(t) &= \hat{H}_1' = -B_1(e^{i\omega t} + e^{-i\omega t}) \hat{h}_1' \equiv \hat{\mu}_z,
\end{align}

obtained when all second order terms in the fields are neglected, as usual; and the Hamiltonian for a pure spin system:

\begin{align}
\hat{H}_0^B &= g_s\mu_0\hat{\vec{s}} \cdot \vec{B}_0, \\
\hat{H}_1^B &= g_s\mu_0\hat{\vec{s}} \cdot \vec{B}_1 (e^{i\omega t} + e^{-i\omega t}).
\end{align}

In both these cases for which the Bloch equation applies, the time-independent and time-dependent parts of the Hamiltonian commute: $[\hat{H}_0^B, \hat{H}_1^B] = 0$, while $[\hat{H}_0, \hat{H}_1] \neq 0$. Either way, the time-independent Hamiltonian can be diagonalized in terms of a complete basis-set $\{|m\rangle\}$:

\begin{equation}
\hat{H}_0|m\rangle = E_m|m\rangle,
\end{equation}

and the time-dependent electron wave function can be written (in the Schrödinger representation) as a linear combination of these basis-set states:

\begin{equation}
|\Psi(t)\rangle = \sum_m c_m(t)e^{-iE_m t/\hbar}|m\rangle,
\end{equation}

with time-dependent coefficients, $c_m(t)$, that satisfy a set of coupled equations,

\begin{equation}
\frac{dc_m}{dt} = -\frac{i}{\hbar} \sum_l e^{-i\omega_{ml} t} \langle m|\hat{H}_1|l\rangle c_l,
\end{equation}

where $\omega_{ml} \equiv (E_l - E_m)/\hbar$. Power is absorbed by the system at the following rate:

\begin{equation}
\mathcal{P}(\omega) = \left[ \frac{dE}{dt}\right]_t = \left[ \frac{d}{dt} \sum_m E_m |c_m|^2 \right]_t
\quad = \sum_m \sum_l \omega_{ml} c_m^* c_l e^{-i\omega_{ml} t} \langle m|\hat{H}_1|l\rangle
\quad = \sum_m \sum_l c_m^* c_l e^{-i\omega_{ml} t} \langle m| -i\hbar \hat{\mu}_z |l\rangle.
\end{equation}

Three different cases can be considered:

- Pure spin system with no coupling to the environment.
- Pure spin system with coupling to the environment.
- Diamagnetic system (magnetic field induced magnetic moment due to orbital angular momentum) with no coupling to the environment.

In the first case of a pure spin system with no coupling to the environment, as well as in the case of the approximate Hamiltonian leading to the regular Bloch equation; $[\hat{H}_0^B, \hat{H}_1^B] = 0$. As a result, the power absorption is identically zero. In this case it would be wrong to apply perturbation theory to the expansion of Eq. (24). This can be understood on very general terms: a time-dependent perturbation which commutes with the time-independent Hamiltonian can not induce transitions.

Different magnetic systems (including in particular pure spin systems) with coupling to the environment were considered in the literature within two basically different approaches. In the first approach, $T_1$ and $T_2$ processes are included when considering the dynamics, and power absorption can thereby occur. The $T_1$ and $T_2$ processes can
be described by relaxation terms added to the Bloch equation; the resulting dynamics can no longer be described by a Hamiltonian.

In another approach introduced by Kubo and coworkers \[4\], which we would like to compare to, it is assumed that a linear-response theory\[4\]. assumed that \( \hat{H}'' \) effectively incorporates the coupling to the environment; although the coupling is not explicitly specified, it is assumed that \( [\hat{H}_0'', \hat{H}_1] \neq 0 \). The power absorption therefore does not vanish, and can be calculated using, for example, a linear-response theory \[4\].

We now show that the power absorption of a diamagnetic system with no coupling to the environment is very similar to power absorption of a pure spin system with coupling to the environment when the coupling to the environment is considered within linear-response theory as in Ref. \[4\]. We show that in both cases the power absorption does not vanish and is given by a similar (though not identical) expression. The similarities and differences are derived and discussed below. The essential point is that as soon as \( [\hat{H}_0', \hat{H}_1] \neq 0 \), power absorption does not vanish, and, using the fact that for realistic magnetic fields \( B_1 \ll B_0 \), time-dependent perturbation theory can be applied.

The first-order solution of Eq. (24) with initial condition at \( t = 0 \), \( c_m(0) = b_m \), is:

\[
c_m = b_m + \frac{1}{\hbar} B_1 \sum_i \langle m|\hat{h}_1|i \rangle \left[ \frac{e^{i(\omega - \omega_{lm})t} - 1}{\omega - \omega_{lm}} - \frac{e^{-i(\omega - \omega_{lm})t} - 1}{\omega - \omega_{ml}} \right]\ b_i .
\]

(30)

Substituting this result into Eq. (29), and applying the rotating wave approximation in the usual way, the power absorption is obtained:

\[
\mathcal{P}(\omega) = 2B_1^2 \sum_{E_n > E_m} \frac{\omega_{nm}}{\hbar} |\langle n|\hat{h}_1|m \rangle|^2 \left( |b_m|^2 - |b_n|^2 \right) \left[ \frac{\sin(\omega - \omega_{nm})t}{\omega - \omega_{nm}} \right] t .
\]

(31)

In the limit \( t \to \infty \), we find:

\[
\mathcal{P}(\omega) = 2B_1^2 \omega \chi''_x ,
\]

(32)

\[
\chi''_x = \pi \sum_{m,n} |\langle n|\hat{h}_1|m \rangle|^2 \left( |b_m|^2 - |b_n|^2 \right) \delta(E_n - E_m - \hbar \omega) .
\]

(33)

In the case of a pure spin system with coupling to the environment \( \hat{h}_1 = \hat{\mu}_x \). Eq. (33) gives the static magnetic susceptibility and with Eq. (32) is identical to the results obtained by Kubo and Nagamiya \[4\] in their Eqs. (18.4) and (19.17). We note that they have obtained this result within a different treatment, using a density matrix formalism, but under the same assumptions as those supporting the perturbative treatment we have used, namely, that the system is linear and in a steady-state. In the density matrix treatment, \( |b_m|^2 \) and \( |b_n|^2 \) in Eq. (33) are replaced by the densities \( \rho(E_m) \) and \( \rho(E_n) \), respectively.

We note here that this expression for the power absorption is correct only as long as a perturbative treatment is appropriate. As soon as a significant part of the population occupies the excited states a nonperturbative treatment would be necessary. The power absorption would necessarily cease as the system continues to absorb energy from the field and evolves to higher energy states if no coupling to the environment were present, but this is not contained in a perturbation theory or linear response approach. Here we study the power absorption only within the perturbative regime. We note that the time scale from turning on the fields till a significant change in the population could be noticed can in principle be quite large.

In the case considered here, of no coupling to the environment but inclusion of orbital effects, \( \hat{h}_1 = \frac{q_0}{2m}(\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) + \frac{q^2}{4m} B_0 \hat{x} \hat{z} \), while in the case of coupling to the environment but no orbital effects, \( \hat{h}_1 = \hat{\mu}_x = \frac{q}{2m}(\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \). Moreover, the spectrum and hence the resonance frequencies are different in these two cases. In either case, once the Bloch equation is modified, whether by relaxation terms or by terms of second order in the external fields, power absorption can ensue. Furthermore, while the numerical details of this power absorption may differ, the general behavior is the same in these two cases. The power absorption is given by Eq. (12) with a somewhat different quantum susceptibility in the two cases. In both cases, the quantum susceptibility is obtained by substituting the appropriate energy eigenvalues and coupling Hamiltonians into Eq. (13).
To summarize this section: focusing on the regime where a linear response theory applies, we have solved for the power absorption using time-dependent perturbation theory. We have derived Eqs. (32, 33) for the power absorption and for the susceptibility. This result is similar to that obtained by Kubo and coworkers in Ref. [1], but there are several differences: the coupling Hamiltonian \( \hat{h}_1 \) is different, the quantum susceptibilities of the two systems are slightly different, and the spectral position is shifted. These are small corrections. Their order of magnitude is determined by the ratio between the magnetic energy and the total energy of the system. Hence, it seems that it would be difficult to experimentally observe a difference between the result for the susceptibility obtained using our approach and the standard result for cw applications where a linear response theory applies. The major difference is in justifying the linear response treatment. We have shown that it applies only if \([\hat{H}_0, \hat{H}_1] \neq 0\). This condition for a consistent application of perturbation theory holds in Kubo’s derivation only if coupling to the environment is included, while for our case here no such coupling is required.

V. POWER ABSORPTION OF AN ELECTRON BOUND IN A \( p \)-ATOMIC-ORBITAL

As an example, we study power absorption of an electron bound by the Coulomb potential, \( V(r) = -Ze^2/(4\pi\epsilon_0r) \), in a \( p \)-orbital (\( l = 1 \)), and placed in the external time-dependent magnetic field of Eq. (2). Neglecting spin effects, the complete Hamiltonian can be written as above. As a basis set we choose the three wave functions:

\[
\langle \vec{r}|\psi_{\pm}\rangle = \pm \frac{1}{\sqrt{2}} (x \pm iy) f(r) , \quad \langle \vec{r}|\psi_0\rangle = z f(r) ,
\]

where for principal quantum number \( n = 2 \),

\[
f(r) \equiv \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{5/2} \exp \left[ -\frac{Z}{2a_0} r \right] ,
\]

and the Bohr radius is defined as \( a_0 \equiv 4\pi\epsilon_0 \hbar^2/(me^2) \). These basis functions are eigenfunctions of the free Hamiltonian when no magnetic fields are present, as well as of \( \hat{H}_0' \), (but not of \( \hat{H}_0 \) or even \( \hat{H}_0 \)). The \( l = 1 \) manifold spanned by this basis set is not closed under the complete Hamiltonian. The orbital angular momentum \( \ell \) is not a good quantum number due to the terms in the Hamiltonian of second order in the external magnetic field, which do not commute with the angular momentum operator. The coupling to other manifolds is small, however, and the energy difference between the different manifolds is large. We therefore neglect the coupling to other manifolds, and consider the action of \( \hat{H} \) only within the \( \ell = 1 \) subspace. A general solution of the time-dependent problem is then given by

\[
|\Psi(t)\rangle = c_0(t)e^{-iE_0t/\hbar}|\psi_0\rangle + c_+(t)e^{-iE_+t/\hbar}|\psi_+\rangle + c_-(t)e^{-iE_-t/\hbar}|\psi_-\rangle ,
\]

and the time-dependent perturbative analysis of the coefficients of the previous section applies with \( m = 0, +, - \).

The diagonal matrix elements of \( \hat{H} \) in this basis set are:

\[
E_0 \equiv \langle \psi_0|\hat{H}_0|\psi_0\rangle = -\frac{\mathcal{E}}{8} + \frac{12}{\mathcal{E}} (\mu_0B_0)^2 ,
\]

\[
E_{\pm} \equiv \langle \psi_{\pm}|\hat{H}_0|\psi_{\pm}\rangle = -\frac{\mathcal{E}}{8} \pm \mu_0B_0 + \frac{15}{\mathcal{E}} (\mu_0B_0)^2 ,
\]

where \( \mathcal{E} \equiv \frac{Z^2e^2}{4\pi\epsilon_0a_0} \). The level spacings are given by,

\[
h\omega_+ \equiv E_+ - E_0 = \mu_0B_0 \left( 1 + 3\frac{\mu_0B_0}{\mathcal{E}} \right) > 0 ,
\]

\[
h\omega_- \equiv E_0 - E_- = \mu_0B_0 \left( 1 - 3\frac{\mu_0B_0}{\mathcal{E}} \right) > 0 ,
\]

where \( h\omega_+ > 0 \) assuming \( 3\mu_0B_0 < \mathcal{E} \). The oscillating field couples \(|\psi_0\rangle\) and \(|\psi_{\pm}\rangle\):

\[
\langle \psi_0|\hat{h}_1|\psi_{\pm}\rangle = \langle \psi_{\pm}|\hat{h}_1|\psi_0\rangle = -\frac{\mu_0}{\sqrt{2}} \left[ 1 \mp 12\frac{\mu_0B_0}{\mathcal{E}} \right] .
\]

The leading order contribution to the power absorption is:
\[ P_0(\omega) = \frac{\pi}{\hbar^2} \left( \mu_0 B_0 \right) \left( \mu_0 B_1 \right)^2 \times \left\{ \left( \left| b_- \right|^2 - \left| b_0 \right|^2 \right) \delta(\omega - \omega_-) + \left( \left| b_0 \right|^2 - \left| b_+ \right|^2 \right) \delta(\omega - \omega_+) \right\}. \] (41)

The next order correction to this power absorption is:

\[ P_1(\omega) = \frac{24\pi}{\hbar^2} \left( \frac{\mu_0 B_0}{\epsilon} \right) \left( \mu_0 B_0 \right) \left( \mu_0 B_1 \right)^2 \times \left\{ \left( \left| b_- \right|^2 - \left| b_0 \right|^2 \right) \delta(\omega - \omega_-) + \left( \left| b_0 \right|^2 - \left| b_0 \right|^2 \right) \delta(\omega - \omega_+) \right\}. \] (42)

Higher order terms are of third order in \( B_1 \). At temperature \( T = 0 \), \( b_0 = b_+ = 0 \) and \( b_- = 1 \), and we obtain:

\[ P(\omega) = \frac{\pi}{\hbar^2} \left( \mu_0 B_0 \right) \left( \mu_0 B_1 \right)^2 \left( 1 + \frac{24\mu_0 B_0}{\epsilon} \right) \delta \left[ \omega - \frac{\mu_0 B_0}{\hbar} \left( 1 - 3\frac{\mu_0 B_0}{\epsilon} \right) \right]. \] (43)

Note that for realistic experimental conditions, \( \left( \mu_0 B_1 \right)^2 \) is small enough to justify the perturbative treatment and as a result \( P(\omega) \) is very small.

Realizable magnetic fields are, for example, \( B_0 = 5 \) T and \( B_1 = 5 \times 10^{-4} \) T. The relative strength of the correction term \( P_1 \) as compared to the leading order term \( P_0 \), is determined by the dimensionless parameter \( 24\mu_0 B_0/\epsilon \), which for \( B_0 = 5 \) T and \( Z = 6 \) (carbon) is equal to \( 1 \times 10^{-5} \). \( P_1 \) as well as the higher order terms are thus but small corrections to \( P_0(\omega) \).

**VI. CONCLUSIONS AND SUMMARY**

In this paper we have studied the dynamics of the gauge-invariant operator for the magnetic dipole moment \( \tilde{\mu} \) of an electronic system in an external magnetic field \( \vec{B} \). In addition to the intrinsic magnetic moment of the electron it includes a field induced magnetic moment arising from the electronic orbital angular momentum, i.e., a diamagnetic contribution. We have derived the Heisenberg equation of motion for this magnetic moment in a general magnetic field and shown that this modified Bloch equation is coupled to two other Heisenberg equations for the position and velocity operators. While we could not solve this set of equations exactly and in closed form, we have solved it perturbatively using time-dependent perturbation theory and calculated the power absorption of the magnetic moment in a time-dependent magnetic field under magnetic-resonance conditions. Under the assumption of a steady-state, we have found an expression for the quantum susceptibility in terms of matrix elements of a coupling Hamiltonian \( \hbar \omega \). Finally, we have explicitly calculated the integrated power absorption for the example of a \( p \)-orbital electron and found that it is given by Eq. (43).

Several generalizations can be easily considered. Upon generalizing to include electron spin, the Hamiltonian and the magnetic moment operator become,

\[ \hat{H} = \hat{V}(r) + \frac{\hat{\Pi}^2}{2m} - \hat{\mu}_s \cdot \vec{B}, \] (44)

\[ \hat{\mu} = \frac{g}{2m} \left( \hat{\vec{r}} \times \hat{\Pi} + g_s \hbar \hat{s} \right) = -\frac{e}{2m} \hat{\vec{r}} \times \hat{\Pi} - g_s \mu_0 \hat{s}, \] (45)

respectively, where \( \hat{\mu}_s = -g_s \mu_0 \hat{s} \), and \( g_s \) is the electron spin gyromagnetic ratio \( (g_s \approx 2.002) \). The last term on the right hand side of Eq. (45) is the intrinsic spin magnetic moment operator of the electron, \( \hat{\mu}_s \). Incorporation of this term into the modified Bloch equation yields the following term on the right hand side of Eq. (44): \(-\frac{\mu_0 g_s}{\hbar} \hat{B} \times \hat{\mu}_s \), i.e., the generalized Bloch equation becomes,

\[ \frac{d\hat{\mu}}{dt} = \frac{e^2}{4m} \left( \hat{\vec{r}} \cdot \frac{\partial \hat{\vec{B}}}{\partial t} \right) \hat{\vec{r}} - \frac{e^2}{2m^2} \left( \hat{\vec{r}} \times \left( \hat{\vec{B}} \times \hat{\Pi} \right) - i\hbar \hat{B} \right) + \frac{(\mu_0 g_s)^2}{\hbar} \hat{B} \times \hat{s}. \] (46)

Inclusion of spin-orbit coupling of the form \( \alpha(\vec{r}) \hat{s} \times \hat{l} \) into the Hamiltonian is also straightforward. The modified Bloch equation then has additional terms on the right hand side proportional to \( \alpha(\vec{r}) \hat{s} \times \hat{l} \) and \( \alpha(s \cdot \vec{r}) (\hat{\vec{B}} \cdot \hat{l}) \). The latter term is due to the magnetically induced magnetic moment. Furthermore, one can also readily include ligand field
effects, exchange coupling effects, etc., within the formulation considered here. Ligand field terms in the Hamiltonian commute with the magnetically induced magnetic moment, as do spin exchange terms, but orbital angular momentum exchange coupling terms do not, and therefore contribute additional terms to the extended Bloch equation due of the magnetically induced magnetic moment.

How do our results differ from previous treatments of magnetic resonance phenomena? It is useful to divide such a comparison into two subjects: the equations of motion and the mechanism of power absorption.

We have shown that the Bloch equation, Eq. (1), is not the correct Heisenberg equation for a magnetic moment $\vec{\mu}$ in the magnetic field $\vec{B}$ when orbital angular momentum is present. A modified Bloch equation, Eq. (4), is obtained. Upon inclusion of spin, the factor of $g_s$ in the term $-\hbar\mu_s/\hbar\bar{B} \times \vec{\mu}_s$, which is equivalent to the last term on the right hand side of Eq. (14), further precludes writing a Bloch equation of the form of Eq. (1) with $\hat{\vec{\mu}} + \hat{\vec{\mu}}_s$. The modified equation can not be written in terms of $\vec{\mu}$ alone. It contains the position and kinetic velocity operators and therefore must be solved together with dynamical equations for these operators. In general, $d\vec{\mu}/dt$ is not perpendicular to $\vec{B}$, and $\vec{\mu}$ oscillates out of phase with $\vec{B}$. This results in a non-vanishing power absorption.

In the usual picture, correct for pure spin systems, power is absorbed only because of the coupling of the spin system to the environment. Without this coupling the magnetic moment $\vec{\mu}$ would oscillate in phase with $\vec{B}$, $d\vec{\mu}/dt$ would be perpendicular to $\vec{B}$ at all times, and no power would be absorbed. Coupling to the environment dephases the oscillations of $\vec{\mu}$ and $\vec{B}$ and induces a nonvanishing component of $d\vec{\mu}/dt$ along $\vec{B}$. In the case considered here, of a magnetic moment that explicitly contains a diamagnetic contribution, the power absorption does not vanish even when coupling to the environment is not included because the magnetic moment has a component which oscillates out of phase with the external field as a result of non-linear terms in the interaction Hamiltonian arising from a magnetic field induced magnetic moment. The phase difference between oscillations of the magnetic field and oscillations of the magnetic dipole moment of a bound electron in this field, is an intrinsic feature of the system and need not be induced by additional couplings to a bath that gives rise to dissipation. This power absorption can be interpreted, as evident from Eq. (14), as being due to the rate of change of the electric dipole moment in the presence of an electric field. Additional power absorption may result due to coupling to a bath.

For cw power absorption, dissipation of energy from the atomic system to the environment is required in order to ensure that the system stays in thermal equilibrium, so that power absorption can be maintained under steady-state conditions. Hence, for truly cw power absorption, as opposed to pulsed magnetic resonance experiments, the two systems depend on coupling to the environment to maintain a steady state and eventually will behave similarly. The results presented here indicate that diamagnetic systems would behave differently from pure-spin systems during the initial time when the turning on of the fields occur. For pure spin systems the time scale for initiation of power absorption would be set by the coupling to the environment while for diamagnetic systems it would be an intrinsic time scale indifferent to the environment. Without a relaxation mechanism, no power would be absorbed by a pure spin system, while the diamagnetic system will absorb power upon the turning on of the fields only until the population of levels reach a new equilibrium. We note that as soon as the population is changed significantly, second and higher order effects become important and a first-order time-dependent perturbation theory would not suffice.

ACKNOWLEDGMENTS

Useful discussions with Garnett Bryant are gratefully acknowledged. This research was supported by The Israel Science Foundation (B. S. is supported by grant No. 181/00 and Y. B. B. by grant No. 212/01).

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