Quantum mechanics of a dipolar ion in a uniform magnetic field

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I investigate the perturbation on the ion cyclotron resonance of an ion in a Penning trap, due to an electric dipole moment. Take for the Hamiltonian a sum of the ionic Hamiltonian H_0, the molecular rotational Hamiltonian H_{rot} and the perturbation from the electric dipole moment H_d. The ionic part is

$$H_0 = \frac{(\vec{p} - e\vec{A})^2}{2M}$$

where the vectors are two-dimensional with $\vec{p} = (\partial/\partial x, \partial/\partial y)/i$. Take the gauge in which

$$\vec{A} = \frac{B_0}{2}(-y, x).$$

This represents magnetic field is in the z direction with strength B_0. Units are such that $\hbar = c = 1$. For the orientational degress of freedom, use the angular momentum representation of the wave function $|l, m\rangle$. The rotational Hamiltonian is diagonal with energy

$$H_{rot}|l, m\rangle = \frac{l(l+1)}{2I}|l, m\rangle$$

where I is the moment of inertia of ion (strictly valid only for linear molecules). The perturbation is

$$H_d = \frac{\vec{p}}{M} \cdot \vec{B} \times \vec{d}$$

where d is the electric dipole operator for the ion in its CM system.

The ionic Hamiltonian H_0 reduces to a harmonic oscillator. We need only consider eigenstates of the form

$$|m\rangle_{ion} = \frac{1}{\sqrt{\pi}a^{m+1}\sqrt{m!}} r^m e^{im\phi} e^{-(r/a)^2/2}.$$

The oscillator length parameter a (with $\hbar$ and c explicit) is given by

$$a = \left(\frac{2\hbar c}{eB_0}\right)^{1/2}$$

The eigenenergies are given by

$$E_m = (m + \frac{1}{2})\omega_c$$

where $\omega_c = eB_0/M$ is the ion cyclotron frequency.

The total wave function is expanded in the product states of $|m_I\rangle_{ion}$ in the ion coordinate and $|l_r, m_r\rangle$ in the orientational coordinate, which we write as

$$|m_T, l_r, m_r\rangle = |m_T - m_r\rangle_{ion}\ |l_r, m_r\rangle.$$

Conservation of azimuthal angular momentum implies that only transitions preserving $m_T = m_I + m_r$ will have nonzero matrix elements.

To compute the perturbation, we need the matrix elements of $\vec{p}$ and $\vec{d}$. The large matrix elements of $\vec{p}$ are

$$\langle m+1|\vec{p}|m\rangle_{ion} = \frac{\sqrt{m+1}}{2a}(i, 1)$$

and its Hermitean adjoint

$$\langle m|\vec{p}|m+1\rangle_{ion} = \frac{\sqrt{m+1}}{2a}(-i, 1).$$

For completeness here are also the matrix element of $\vec{r}$:

$$\langle m+1|\vec{r}|m\rangle_{ion} = \frac{a}{2}\sqrt{m+1}(1, -i).$$

$$\langle m|\vec{r}|m+1\rangle_{ion} = \frac{a}{2}\sqrt{m+1}(1, i).$$

The radius of the cyclotron orbit is

$$R = a\sqrt{m+1}$$

We also need the matrix elements of the dipole operator. These are given by

$$\langle l'm'|\vec{d}|lm\rangle = d_0\sqrt{\frac{2l+1}{2(2l'+1)}}(10l0|l'0)\Big[(11lm|l'm')(-1, i) + (1-1lm|l'm')(1, i)\Big]$$

where d_0 is the intrinsic dipole moment. Assembling these ingredients, the matrix elements of the perturbation are

$$\langle m_T l'm'|H_d|m_T lm\rangle = \frac{iB_0 d_0}{Ma}\sqrt{\frac{2l+1}{2(2l'+1)}}(10l0|l'0)\Big[(11lm|l'm')\sqrt{m_T - m} + (1-1lm|l'm')\sqrt{m_T - m + 1}\Big].$$

The matrix can be simplified in the limit $m_T >> 1$, which is certainly satisfied in practice. In this limit we may eliminate the m_T-dependent factors in favor of the radius of the cyclotron orbit R. The term in square brackets becomes

$$\frac{R}{a}\Big[(11lm|l'm') + (1-1lm|l'm')\Big]$$

This is just the form one would obtain taking the y-component of $\vec{d}$ by itself. Rotating the coordinate system, one also gets the same eigenvalues with a coupling to the z direction only. This simplifies the matrix because then m_r is conserved as well. The nonzero matrix elements of the perturbation in the rotated coordinate system have the form

$$\langle m_T l' m|H_d|m_T l m\rangle = \frac{RB_0 d_0}{Ma^2}\sqrt{\frac{2l+1}{(2l'+1)}}(10l0|l'0)(11lm|l'm).$$

Now consider some limiting cases. We can safely take $\omega_c << 1/I$ in all cases. But the coupling matrix element may be either larger or smaller than $1/I$. If it is much smaller than $1/I$, the the expansion may be truncated with $l_r \leq 1$ The $l_r = 0$ component is dominant and the effect of the $l_r = 1$ component can be computed in second-order perturbation theory. The result for the energy is

$$E(R) = \frac{R^2}{a^2}\omega_c - \frac{R^2 d_0^2 B_0^2 I}{3M^2 a^4}$$

The frequency that would be observed is

$$\omega = E(m_T) - E(m_T - 1) \approx \frac{dE}{dR}\frac{dR}{dm}.$$

One then finds the cyclotron frequency shifted by an amount

$$\frac{\omega}{\omega_c} - 1 \approx -\frac{d_0^2 B_0^2 I}{3M^2 a^2}.$$

The other limit is when the off-diagonal matrix element is much larger than $1/I$. In this case the rotational energy can be neglected and H_d is diagonalized. The lowest eigenvalue is

$$-\frac{RB_0 d_0}{Ma^2}$$

and the corresponding frequency shift is

$$\frac{\omega}{\omega_c} - 1 \approx -\frac{B_0 d_0}{2MR}.$$

Note that in this case there is a continuous spectrum of orientational states with shifts between $\pm B_0 d_0/2MR$.