Physics 232

Gauge invariance of the magnetic susceptibilty

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I. INTRODUCTION

We have seen in class that the following additional terms appear in the Hamiltonian on adding a magnetic field:

$$\Delta\mathcal{H} = \Delta\mathcal{H}_1 + \Delta\mathcal{H}_2 \tag{1}$$

where

$$\boxed{\Delta\mathcal{H}_1 = \frac{e}{2mc}\left(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}\right),} \tag{2}$$

$$\boxed{\Delta\mathcal{H}_2 = \frac{e^2}{2mc^2}\,\mathbf{A}^2,} \tag{3}$$

where $\mathbf{A}$ means $\mathbf{A}(\mathbf{x})$, i.e. the value of the vector potential *at the position of the electron*. Note that, except in the "Coulomb gauge" where $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$, $\mathbf{A}(\mathbf{x})$ does not commute with $\mathbf{p}$ and so we need to keep the order $\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}$ in $\Delta\mathcal{H}_1$.

For simplicity of notation, we consider here just single electron, but the discussion is easily generalized to many electrons simply by incorporating a sum over the electrons.

We consider here a time-independent magnetic field. For the case of a uniform field we chose, in class, the following gauge

$$\mathbf{A} = -\frac{1}{2}\mathbf{x}\times\mathbf{H}\,, \tag{4}$$

where $\mathbf{H}$ is the applied field. This is a particularly convenient gauge because we showed in class that, in it,

$$\Delta\mathcal{H}_1 = \frac{e\hbar}{2mc}\mathbf{L}\cdot\mathbf{H}\,, \tag{5}$$

which I call the "paramagnetic" contribution, and which vanishes for closed shell atoms where the total orbital angular momentum $\mathbf{L}$ is zero. In this gauge, the remaining piece, $\Delta\mathcal{H}_2$, which I call the "diamagnetic" contribution, is small and negative.

In a gauge transformation we make the replacement

$$\boxed{\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla}\chi\,,} \tag{6}$$

where $\chi(\mathbf{x})$ is any function of $\mathbf{x}$. This transformation clearrly leaves the value of the field $\mathbf{H}$ unchanged but gives rise to the following additional terms in the Hamiltonian:

$$\Delta\mathcal{H}_{\text{gauge}} = \frac{e}{2mc}\left(\mathbf{p}\cdot\boldsymbol{\nabla}\chi + \boldsymbol{\nabla}\chi\cdot\mathbf{p}\right) + \frac{e^2}{2mc^2}\left(2\boldsymbol{\nabla}\chi\cdot\mathbf{A} + (\boldsymbol{\nabla}\chi)^2\right)\,. \tag{7}$$

However, the $\boxed{\text{final answer to any calculation should be gauge invariant}}$, i.e. independent of these extra terms involving χ.

In this handout we shall show explicitly that the magnetic susceptibility is gauge invariant. The susceptibility requires the change in the free energy up to second order in the field, or equivalently, up to second order in $\mathbf{A}$. The free energy is given by

$$F = -k_B T \log Z = -k_B T \log \sum_n e^{-\beta E_n}\,. \tag{8}$$

Hence if we can show that the energy levels are inpendendent of the gauge function χ up to second order, we will have shown that the susceptibility is gauge invariant.

II. THE SUSCEPTIBILITY

Let us denote an energy eigenstate of the unperturbed Hamiltonian (i.e. in the absence of a field) by $|n\rangle$ and its energy by E_n. To determine the change in an energy level $|k\rangle$ up to second order in the field we need to treat $\Delta\mathcal{H}_2$ to first order in perturbation theory (because it is already second order in the field), and $\Delta\mathcal{H}_1$ to second order (because it is only first order in the field). Hence, if we take some gauge, the change in E_k on adding the field is given by

$$\Delta E_k = \frac{e}{2mc}\langle k|\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}|k\rangle + \frac{e^2}{2mc^2}\langle k|\mathbf{A}^2|k\rangle + \frac{e^2}{(2mc)^2}\sum_{n\neq k}\frac{|\langle k|\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}|n\rangle|^2}{E_k - E_n}\,. \tag{9}$$

Now suppose we do a gauge transformation. The additional terms in Eq. (7) are then added to the Hamiltonian, but they should not change ΔE_k. In other words we should find that

$$
\begin{aligned}
0 \;=\; & \Delta E_k^{\rm gauge} = && (10)\\
& \frac{1}{2mc}\langle k|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|k\rangle && (11)\\
+\; & \frac{e^2}{mc^2}\langle k|\boldsymbol{\nabla}\chi\cdot\mathbf{A}|k\rangle && (12)\\
+\; & \frac{e^2}{2mc^2}\langle k|(\boldsymbol{\nabla}\chi)^2|k\rangle && (13)\\
+\; & \frac{e^2}{4m^2c^2}\sum_{n\neq k}\frac{\langle k|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|n\rangle\langle n|\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}|k\rangle}{E_k-E_n} && (14)\\
+\; & \frac{e^2}{4m^2c^2}\sum_{n\neq k}\frac{\langle k|\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}|n\rangle\langle n|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|k\rangle}{E_k-E_n} && (15)\\
+\; & \frac{e^2}{4m^2c^2}\sum_{n\neq k}\frac{|\langle k|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|n\rangle|^2}{E_k-E_n}\,. && (16)
\end{aligned}
$$

It seems a formidable task to show that these terms add up to zero. However, we will find that it is not as bad as it seems. Furthermore, on the way we will derive a useful result, a special case of which leads to the important $\boxed{f\text{-sum rule.}}$

III. AN IMPORTANT RESULT

We see that many of the terms in $\Delta E_k^{\rm gauge}$ in Eq. (10) involve $\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi$. We now derive an alternative expression for it, which will turn out to be useful. We take the unperturbed Hamiltonian to be

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})\,, \tag{17}$$

so there are no velocity dependent forces in the absence of the magnetic field. The commutator of $\chi(\mathbf{x})$ with $\mathcal{H}$ is given by

$$[\chi,\mathcal{H}] = \frac{1}{2m}[\chi,\mathbf{p}^2] = \frac{1}{2m}[\chi\mathbf{p}^2 - \mathbf{p}(\chi\cdot\mathbf{p}) + \mathbf{p}\cdot(\chi\mathbf{p}) - \mathbf{p}^2\chi] = \frac{1}{2m}\left([\chi,\mathbf{p}]\cdot\mathbf{p} + \mathbf{p}\cdot[\chi,\mathbf{p}]\right)\,. \tag{18}$$

Since $[\chi,\mathbf{p}] = i\hbar\boldsymbol{\nabla}\chi$ we have

$$[\chi,\mathcal{H}] = \frac{i\hbar}{2m}\left(\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi\right) \tag{19}$$

which can be written as

$$\boxed{\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi = -2i\,\frac{m}{\hbar}\,[\chi,\mathcal{H}]\,.} \tag{20}$$

Next we take matrix elements of this equation between states $|k\rangle$ and $|n\rangle$:

$$\langle n|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|k\rangle = -2i\,\frac{m}{\hbar}\,\langle n|\chi\mathcal{H}-\mathcal{H}\chi|k\rangle\,. \tag{21}$$

Since $|n\rangle$ and $|k\rangle$ are exact eigenstates of $\mathcal{H}$ with eigenvalues E_n and E_k, we can write this last expression as

$$\boxed{\langle n|\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi|k\rangle = 2i\,\frac{m}{\hbar}\,(E_n-E_k)\,\langle n|\chi|k\rangle\,,} \tag{22}$$

which will be useful in the remaining sections.

IV. A SPECIAL CASE: THE f-SUM RULE.

To simplify things and to make contact with a well-known result in quantum mechanics, in this section we take the special case

$$\chi(\mathbf{x}) = x_\alpha\,, \tag{23}$$

where α denotes one of the cartesian coordinates. It follows that $\boldsymbol{\nabla}\chi\cdot\mathbf{p}=\mathbf{p}\cdot\boldsymbol{\nabla}\chi=p_\alpha$. Hence Eq. (22) can be written as

$$(E_k-E_n)\,\langle n|x_\alpha|k\rangle = \frac{i\hbar}{m}\langle n|p_\alpha|k\rangle\,. \tag{24}$$

Multiplying by $\langle k|x_\alpha|n\rangle$ gives

$$(E_k-E_n)\,|\langle n|x_\alpha|k\rangle|^2 = \frac{i\hbar}{m}\langle k|x_\alpha|n\rangle\langle n|p_\alpha|k\rangle\,, \tag{25}$$

and interchanging n with k gives

$$(E_k-E_n)\,|\langle n|x_\alpha|k\rangle|^2 = -\frac{i\hbar}{m}\langle k|p_\alpha|n\rangle\langle n|x_\alpha|k\rangle\,. \tag{26}$$

Adding Eqs. (25) and (26), summing over n, and dividing by 2, gives

$$\begin{aligned}\sum_n (E_n-E_k)\,|\langle n|x_\alpha|k\rangle|^2 &= -\frac{i\hbar}{2m}\sum_n\left(\langle k|x_\alpha|n\rangle\langle n|p_\alpha|k\rangle-\langle k|p_\alpha|n\rangle\langle n|x_\alpha|k\rangle\right)\\ &= -\frac{i\hbar}{2m}\langle k|x_\alpha p_\alpha-p_\alpha x_\alpha|k\rangle = \frac{\hbar^2}{2m}\,,\end{aligned} \tag{27}$$

where we used the completeness of the eigenstates $\sum_n |n\rangle\langle n| = 1$. Our result is therefore

$$\boxed{\sum_n (E_n-E_k)\,|\langle n|x_\alpha|k\rangle|^2 = \frac{\hbar^2}{2m}} \tag{28}$$

which is known as the f-sum rule. It plays an important rule in atomic and solid state physics. The key assumption made in deriving it is the absence of velocity-dependent forces.

It is of interest to verify that the f-sum rule works for the simple harmonic oscillator. For that model we have $E_k = (k+1/2)\hbar\omega$, $\langle k|x|k+1\rangle = \sqrt{\hbar/2m\omega}\,\sqrt{k+1}$, and $\langle k|x|k-1\rangle = \sqrt{\hbar/2m\omega}\,\sqrt{k}$, so the left hand side of Eq. (28) is equal to

$$\hbar\omega\,\frac{\hbar}{2m\omega}\,(k+1) + (-\hbar\omega)\,\frac{\hbar}{2m\omega}\,k = \frac{\hbar^2}{2m} \tag{29}$$

as required.

If one multiplies Eq. (24) by $\langle k|p_\alpha|n\rangle$ rather than by $\langle k|x_\alpha|n\rangle$ and then follows the similar steps to those above, one finds a sum rule for the moments of the momentum

$$\sum_{n\neq k} \frac{|\langle n|p_\alpha|k\rangle|^2}{E_n - E_k} = \frac{m}{2}\,. \tag{30}$$

(The term with $n = k$ can be omitted because $\langle k|p|k\rangle = 0$ according to Eq. (24).)

Incidentally, if we had not taken the special case $\chi(\mathbf{x}) = x_\alpha$ but had kept a general form for $\chi(\mathbf{x})$, and used similar reasoning, we would have obtained the following "generalized f-sum rule":

$$\boxed{\sum_n (E_n - E_k)\,|\langle n|\chi(\mathbf{x})|k\rangle|^2 = \frac{\hbar^2}{2m}\,\langle k|(\boldsymbol{\nabla}\chi)^2|k\rangle.} \tag{31}$$

V. GAUGE INVARIANCE OF THE SUSCEPTIBILITY

We now show that a gauge transformation gives no change in the susceptibility, i.e. the sum of the terms for $\Delta E_k^{\rm gauge}$ in Eq. (22) is zero.

First of all consider Eq. (11). According to Eq. (22) with $n = k$ $\boxed{\text{Eq. (11) is equal to zero.}}$

Next, substituting Eq. (22) into Eq. (14) (with n and k interchanged) gives

$$\frac{e^2}{4m^2c^2}\,\frac{2im}{\hbar}\,\sum_n \langle k|\chi|n\rangle\langle n|\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}|k\rangle = \frac{ie^2}{2\hbar mc^2}\langle k|\chi(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A})|k\rangle\,. \tag{32}$$

Similarly Eq. (15) becomes

$$-\frac{ie^2}{2\hbar mc^2}\langle k|(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A})\chi|k\rangle\,. \tag{33}$$

Combining Eqs. (32) and (33) gives

$$\begin{aligned} \frac{ie^2}{2\hbar mc^2}\langle k|\chi(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) - (\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A})\chi|k\rangle &= \frac{ie^2}{2\hbar mc^2}\langle k|[\chi,\mathbf{p}]\cdot\mathbf{A} + \mathbf{A}[\chi,\mathbf{p}]|k\rangle \\ &= -\frac{e^2}{mc^2}\langle k|\boldsymbol{\nabla}\chi\cdot\mathbf{A}|k\rangle, \end{aligned} \tag{34}$$

which cancels Eq. (12). Hence we have found that $\boxed{\text{Eqs. (12), (14) and (15) sum to zero.}}$

Next substitute Eq. (22) for the left hand factor in Eq. (16). This gives

$$\frac{ie^2}{2\hbar mc^2}\langle k|\chi(\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi)|k\rangle\,. \tag{35}$$

Alternatively we could have substituted for the right hand factor in Eq. (16) obtaining

$$-\frac{ie^2}{2\hbar mc^2}\langle k|(\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi)\chi|k\rangle\,. \tag{36}$$

Taking the average of Eqs. (35) and (36), Eq. (16) can be written as

$$\begin{aligned}\frac{ie^2}{4\hbar mc^2}\langle k|\chi(\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi)-(\boldsymbol{\nabla}\chi\cdot\mathbf{p}+\mathbf{p}\cdot\boldsymbol{\nabla}\chi)\chi|k\rangle &= \frac{ie^2}{4\hbar mc^2}\langle k|[\chi,\mathbf{p}]\cdot\boldsymbol{\nabla}\chi+\boldsymbol{\nabla}\chi[\chi,\mathbf{p}]|k\rangle \\ &= -\frac{e^2}{2mc^2}\langle k|(\boldsymbol{\nabla}\chi)^2|k\rangle,\end{aligned} \tag{37}$$

which cancels Eq. (13). Hence we have shown that $\boxed{\text{Eqs. (13) and (16) sum to zero.}}$

Altogether we have shown in this section that Eqs. (11)–(16) sum to zero. Hence

$$\boxed{\text{the susceptibility does not depend on choice of gauge}}$$

as expected on general grounds.