How to treat directly magnetic fields in first-principle calculations and the possible shape of the Lagrangian

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This work checks the Pauli equation with the description of the magnetic field and found a possible missing term in it. We propose a fixed Pauli equation, where the application in density functional theory explains the observed magnetic susceptibilities for Al, Si, and Au with applying directly magnetic fields. The possible shape of the Lagrangian describing the charged particle with an external magnetic field is also discussed.

Our textbooks give us many theories describing the world, which are Maxwell equations, Schrödinger equations, and Dirac equations, for example. These are until now continuing to explain our experimental observations. However, if we found some inconsistencies between theories and observations, it is a big chance to open the door for a physics no one knows.

Let us see our history to find which issue people are in trouble about. One of not solved problems is how to treat the magnetic field, in which we still do not know the universal method to reproduce both the paramagnetism and diamagnetism for solid states including metals. The historical starting point of considering theoretically the magnetic field is Pauli equation[1], from which Landau[2] and Wilson[3] discussed about the way of calculating magnetic susceptibilities in the diamagnetism. Thanks to their works, many theoretical results of the magnetic susceptibilities in both model[4–8] and density functional theory (DFT)[9, 10] have been explaining the experimental observations until now. However, no one applies *directly* the magnetic field to get the diamagnetism for solids in DFT. In this paper, a problem in the current theory is discovered and fixed to be able to treat the magnetic field properly in solids.

In 1950's, Wilson[3] and Ginzburg[11] are discussing, respectively, diamagnetism and superconductivity with using the Hamiltonian

$$\frac{1}{2m}\left(\hat{\mathbf{p}}+q\mathbf{A}\right)^2+qV, \tag{1}$$

where m is electron mass, $\hat{\mathbf{p}}=-i\hbar\,\nabla$ is the momentum operator, $q=-e$ is the electron charge defined by the absolute value $e>0$, $\mathbf{A}$ is the vector potential satisfying $\nabla\times\mathbf{A}=\mathbf{B}$ with the magnetic field $\mathbf{B}$, and V is the electro-static potential. More recently, the diamagnetic susceptibilities of atoms based on DFT are calculated from this Hamiltonian.[12] However, the analytical mechanics produces for us the vector potential with the opposite sign in the Hamiltonian

$$\frac{1}{2m}\left(\hat{\mathbf{p}}-q\mathbf{A}\right)^2+qV, \tag{2}$$

in which the paramagnetism was explained.

In the analytical mechanics, from the Lorentz force $q\,\mathbf{v}\times\mathbf{B}$ with the velocity of the particle $\mathbf{v}$, we somehow derived the potential

$$U=-q\mathbf{A}\cdot\mathbf{v}+qV, \tag{3}$$

and which makes the Lagrangian

$$L=T-U=\frac{1}{2}m\mathbf{v}^2+q\mathbf{A}\cdot\mathbf{v}-qV. \tag{4}$$

The momentum becomes

$$\mathbf{p}=\frac{\partial}{\partial\mathbf{v}}L=m\mathbf{v}+q\mathbf{A}, \tag{5}$$

and the Hamiltonian becomes

$$\begin{aligned} H &= \left(\mathbf{v}\cdot\frac{\partial}{\partial\mathbf{v}}-1\right)L \\ &= \frac{1}{2}m\mathbf{v}^2+qV \\ &= \frac{1}{2m}\left(\mathbf{p}-q\mathbf{A}\right)^2+qV, \end{aligned} \tag{6}$$

which is consistent with the Hamiltonian (2). The motion equation is

$$\begin{aligned} \mathbf{0} &= \left(\frac{\partial}{\partial t}\frac{\partial}{\partial\mathbf{v}}-\frac{\partial}{\partial\mathbf{r}}\right)L \\ &= m\dot{\mathbf{v}}-q\left(\mathbf{v}\times\mathbf{B}-\nabla V\right), \end{aligned} \tag{7}$$

where the symmetric gauge $\mathbf{A}=\mathbf{B}\times\mathbf{r}\,/\,2$ is used. Then, we constructed the Pauli equation

$$\frac{1}{2m}\left\{\sigma\cdot\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\right\}^2\psi=\left(\hat{E}-qV\right)\psi, \tag{8}$$

where σ is Pauli matrices

$$\{\sigma_x,\sigma_y,\sigma_z\}=\left\{\begin{pmatrix} & 1\\ 1 & \end{pmatrix},\begin{pmatrix} & -i\\ i & \end{pmatrix},\begin{pmatrix} 1 & \\ & -1\end{pmatrix}\right\}, \tag{9}$$

the other values are implicitly multiplied by the unit matrix

$$\sigma_0=\begin{pmatrix} 1 & \\ & 1\end{pmatrix}=1, \tag{10}$$

ψ is an one-electron wavefunction, and $\hat{E}=i\hbar\partial_t$ is the time differential operator. The left-hand side becomes

$$\left\{\frac{\hat{\mathbf{p}}^2}{2m}-\frac{q}{2m}\mathbf{B}\cdot\left(\hat{\mathbf{l}}+\hbar\sigma\right)\right\}\psi+O\left(\mathbf{B}^2\right), \tag{11}$$

where $\hat{\mathbf{l}} = \mathbf{r} \times \hat{\mathbf{p}}$ is the angular momentum operator, and the $\mathbf{B}$ first-order terms are indicating the paramagnetism.

About the potential (3), we notice that the particle likes to have $\mathbf{v}$ parallel to $q\mathbf{A}$ with the Lorentz force pointing the outside

$$\begin{aligned} & q\mathbf{v} \times \mathbf{B} \\ \propto \; & q^2 \mathbf{A} \times \mathbf{B} = q^2 \frac{\mathbf{B} \times \mathbf{r}}{2} \times \mathbf{B} = \frac{(\mathbf{B} \cdot \mathbf{B})\,\mathbf{r} - (\mathbf{r} \cdot \mathbf{B})\,\mathbf{B}}{2/q^2}. \end{aligned} \tag{12}$$

So in the above Lagrangian (4), the charged particle can not make the bound state as the cyclotron motion in the magnetic field.

Since the Lagrangian tells us many informations like the Hamiltonian, the force, and the momentum, it is not reasonable to create the Lagrangian from only information of the Lorentz force. Therefore, it is better for us to change the strategy of understanding the magnetic field. Let us try to construct one candidate of the Hamiltonian explaining experimental observations. Current our agreements are followings. (i) The charged particle moves with the Lorentz force and behaves as the diamagnetism in a magnetic field. (ii) The dipole moments like usual magnets behave as the paramagnetism with each others. The vector potential includes $\mathbf{B} \times \mathbf{r}$, where the vector $\mathbf{r}$ seems to connect the magnetic field $\mathbf{B}$ and the particle surrounding it with the cyclotron motion. On the other hand, usual magnets attract or repulse with each others at positions of those poles, where $\mathbf{B} \cdot \mathbf{r}$ becomes dominant and is expected to be a missing term to explain the paramagnetism. Based on the relation

$$(\sigma \cdot \mathbf{B})\,(\sigma \cdot \mathbf{r}) = \mathbf{B} \cdot \mathbf{r} + i\sigma \cdot \mathbf{B} \times \mathbf{r}, \tag{13}$$

we may be able to consider the following fixed Pauli equation

$$\frac{1}{2m} \left\{ \sigma \cdot (\hat{\mathbf{p}} + q\mathbf{A}) - 2qi\,(\mathbf{B} \cdot \mathbf{r}) \right\}^2 \psi = \left(\hat{E} - qV \right) \psi. \tag{14}$$

Then, the left-hand side becomes

$$\left\{ \frac{\hat{\mathbf{p}}^2}{2m} + \frac{q}{2m} \mathbf{B} \cdot \left(\hat{\mathbf{l}} - \hbar\sigma \right) - 4qi\,(\mathbf{B} \cdot \mathbf{r})\,(\sigma \cdot \hat{\mathbf{p}}) \right\} \psi + O\left(\mathbf{B}^2\right). \tag{15}$$

Here, we see that the orbital and spin parts of Zeeman term work as, respectively, the diamagnetism and the paramagnetism, although an unknown extra term is appearing in the $\mathbf{B}$ first-order terms. To understand the extra term, let us consider the one-dimension problem with the magnetic field pointing the z direction. If we prepare an s orbital as ψ, then with being careful for only the sign, the extra term becomes

$$-4q\hbar B_z z \sigma_z \partial_z \psi \propto qB_z z \sigma_z z \psi \propto qB_z \sigma_z \psi, \tag{16}$$

which seems to work as the diamagnetism.

The Pauli equation is changing to the following equation

$$\frac{1}{2m} \left\{ \sigma \cdot (\hat{\mathbf{p}} + q\mathbf{A}) + qX \right\}^2 \psi = \left(\hat{E} - qV \right) \psi, \tag{17}$$

where X is the extra term $-2i\ \mathbf{B} \cdot \mathbf{r}$. We note that changing $q\mathbf{A} \to q\mathbf{A} - \hbar\nabla f$, $qV \to qV - \hbar\partial_t f$, and $\psi \to e^{if}\ \psi$ does not change the equation. This is the usual gauge symmetry keeping the norm $|\psi|$. We also find a symmetry for spin coordinates

$$qX \;\to\; qX - \lambda, \tag{18}$$

$$\psi \;\to\; \begin{pmatrix} e^{i\lambda z} & \\ & e^{-i\lambda z} \end{pmatrix} \psi, \tag{19}$$

which is not yet appearing in the classical physics.

Table I shows the DFT results adopting (15) for the face-centered-cubic structured Al, Si, and Au with the experimentally observed crystal structures[13]. By applying directly 0.1 T for [111], [110], and [001] directions, molar magnetic susceptibilities are evaluated and are consistent with the experiments[14], although we have to check more materials.

TABLE I: Calculated molar magnetic susceptibilities (10^{-6}cm^3/mol) and the experimental values[14].

	Our results	Expt.
Al	7	16.5
Si	-4	-3.12
Au	-15	-28

Hereafter, we discuss about an possibility of the shape of the Lagrangian describing the charged particle in a magnetic field. Not to have inconsistencies in the motion equation appearing later, we have to define a four dimensional space including an unknown ξ axis. The coordinate is

$$(\mathbf{r}, i\xi) = \sigma \cdot \mathbf{r} + i\xi, \tag{20}$$

where the local velocity becomes

$$(\mathbf{v}, iv_\xi) = \sigma \cdot \mathbf{v} + iv_\xi = \sigma \cdot \frac{\partial \mathbf{r}}{\partial t} + i\frac{\partial \xi}{\partial t}. \tag{21}$$

Then, we define the kinetic energy

$$T = \frac{m}{2} \left\{ (\sigma \cdot \mathbf{v})^2 - v_\xi^2 \right\}. \tag{22}$$

By using this, one candidate of the Lagrangian satisfying the Hamiltonian (14) and the Lorentz force is

$$\begin{aligned} L \;=\; & \frac{m}{2} \left\{ (\sigma \cdot \mathbf{v})^2 - v_\xi^2 \right\} \\ & + \frac{qi}{4} (\sigma \cdot \mathbf{v})\,(\sigma \cdot \mathbf{r})\,(\sigma \cdot \mathbf{B}) \\ & - \frac{5qi}{4} (\sigma \cdot \mathbf{B})\,(\sigma \cdot \mathbf{v})\,(\sigma \cdot \mathbf{r}) - qV, \end{aligned} \tag{23}$$

where the momentum becomes

$$
\begin{aligned}
\sigma \cdot \mathbf{p} &= \left(\sigma \cdot \frac{\partial}{\partial \mathbf{v}}\right) L \\
&= \sigma \cdot m\mathbf{v} + \frac{3qi}{4}\left(\sigma \cdot \mathbf{r}\right)\left(\sigma \cdot \mathbf{B}\right) \\
&\quad + \frac{5qi}{4}\left(\sigma \cdot \mathbf{B}\right)\left(\sigma \cdot \mathbf{r}\right) \\
&= \sigma \cdot m\mathbf{v} + 2qi\left(\mathbf{B} \cdot \mathbf{r}\right) - \sigma \cdot q\mathbf{A}, \qquad (24)
\end{aligned}
$$

and

$$
ip_\xi = \frac{\partial}{\partial iv_\xi} L = imv_\xi. \qquad (25)
$$

The Hamiltonian becomes

$$
\begin{aligned}
H &= \left(\mathbf{v} \cdot \frac{\partial}{\partial \mathbf{v}} + iv_\xi \frac{\partial}{\partial iv_\xi} - 1\right) L \\
&= \frac{m}{2}\left\{\left(\sigma \cdot \mathbf{v}\right)^2 - v_\xi^2\right\} + qV \\
&= \frac{1}{2m}\left[\left\{\sigma \cdot \left(\mathbf{p} + q\mathbf{A}\right) - 2qi\left(\mathbf{B} \cdot \mathbf{r}\right)\right\}^2 - p_\xi^2\right] + qV, \qquad (26)
\end{aligned}
$$

which is consistent with the Hamiltonian (14) if the coordinate system is chosen to have the constant momentum p_ξ. The motion equation becomes

$$
\begin{aligned}
0 &= \left\{\frac{\partial}{\partial t}\frac{\partial}{\partial iv_\xi} - \frac{\partial}{\partial i\xi} + \sigma \cdot \left(\frac{\partial}{\partial t}\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{r}}\right)\right\} L \\
&= im\dot{v}_\xi + \sigma \cdot m\dot{\mathbf{v}} \\
&\quad + 2qi\left(\mathbf{B} \cdot \mathbf{v}\right) - \sigma \cdot q\frac{\mathbf{B} \times \mathbf{v}}{2} + \sigma \cdot q\frac{\partial V}{\partial \mathbf{r}} \\
&\quad + \frac{qi}{4}\left(\sigma \cdot \mathbf{v}\right)\left(\sigma \cdot \mathbf{B}\right) + \frac{5qi}{4}\left(3\mathbf{v} \cdot \mathbf{B} + i\sigma \cdot \mathbf{v} \times \mathbf{B}\right) \\
&= i\left\{m\dot{v}_\xi + 6q\left(\mathbf{v} \cdot \mathbf{B}\right)\right\} + \sigma \cdot \left\{m\dot{\mathbf{v}} - q\left(\mathbf{v} \times \mathbf{B} - \nabla V\right)\right\}, \qquad (27)
\end{aligned}
$$

where if the charged particle has the velocity parallel to the magnetic field, the particle will be accelerated along the ξ axis. We emphasize that this Lagrangian is still in a fantasy, because there is no proof from the experimental side.

Summarizing, we found a possible missing term in the description of the magnetic field of the Pauli equation. Then, the fixed Pauli equation explains Al, Si, and Au for the experimental magnetic susceptibilities. The results are reasonable in both the paramagnetic and diamagnetic materials including metals at the moment. The possible shape of the Lagrangian for the charged particle in the magnetic field is also discussed.

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