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# Electron-corrected Lorentz forces in solids and molecules in a magnetic field

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We describe the effective Lorentz forces acting on the ions of a generic insulating system in a magnetic field, in the context of Born-Oppenheimer *ab initio* molecular dynamics. The force on each ion includes an important contribution of electronic origin, which depends explicitly on the velocity of all other ions. It is formulated in terms of a Berry curvature, in a form directly suitable for future first principles classical dynamics simulations based, e.g., on density functional methods. As a preliminary analytical demonstration we present the dynamics of an $H_2$ molecule in a field of intermediate strength, approximately describing the electrons through Slater's variational wave function.

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Understanding the behavior of matter in large magnetic fields is important both conceptually and practically. The effect of a magnetic field on a nonmagnetic (molecular, fluid or solid) electronic insulator is twofold. The first is on the electronic states, via a field induced modification of electron quantization. The states of free electrons in a magnetic field are split into Landau levels; in a general insulator, the electronic states or bands will turn into some generalized form of Landau levels, whose splittings are important when at large fields they become comparable with band gaps. These electronic effects can be efficiently calculated with modern density functional theory (DFT) methods well described in the literature.[1] The second type of field effects, important in dynamics, are those on nuclear motion, via Lorentz forces. In an insulating or closed shell system, where electron motion can be decoupled adiabatically, the effective Lorentz force $\boldsymbol{F}_n$ on any ion $n$ still depends on the electronic states. Schematically, the total effective Lorentz force may range between the bare Lorentz force $\boldsymbol{F}_n=(Q_n/c)\boldsymbol{V}_n\times\boldsymbol{B}$ (if electrons could be ignored) to zero (if electrons could be assumed to be tightly bound to nuclei, thus neutralizing them). Even if the effect on the electronic structure is very small and probably negligible for solid state applications, the electronic contribution to the Lorentz force is not negligible at all, but is so far without a clear understanding of how one may, at least in principle, calculate it.

A pioneering fully quantum-mechanical treatment of nuclei and electrons in a magnetic field was formulated long ago, establishing a clear basis of principle.[2,3] The separation of the center-of-mass nuclear motion gives rise, apart from a trivial motional Stark effect, to a number of mass-correction terms in the electronic and nuclear Hamiltonians, which provide additional couplings of the motion of different nuclei. Unfortunately, this approach is computationally very demanding and can be applied at best to small molecules or clusters. There exists to our knowledge neither an explicit formulation that can be used right away for *ab initio* simulations, for example, of DFT type, nor a direct application to real systems, beyond the hydrogen atom.[4]

In this paper we pursue a formulation of electronic Lorentz forces based on the Born-Oppenheimer (BO) approximation, in principle suitable for state-of-the-art first principles simulations. As an illustration, we apply it to the dynamics in a magnetic field of the $H_2$ molecule described by a simple variational wave function. Following Refs. 4 and 5, we will use the electronic Berry phases as a tool to calculate electronic Lorentz forces acting on the ions in a general insulating system. The BO approximation, which amounts to assume fixed and infinite mass nuclei, is made before the separation of the center-of-mass motion. By these assumptions we neglect the motional Stark effect and the mass correction terms. The former is well justified as long as the particle speed is small compared to the speed of light, as in most condensed systems.[6] Mass correction terms become important for exceedingly strong magnetic fields, when the insulating character may be lost and/or particles may behave relativistically, in which case these corrections should of course be included in the nuclear and electronic Hamiltonian.

We assume the ground state electronic wave function to be given, at each time step, by an electronic structure calculation, such as Hartree-Fock,[7] or density functional theory methods.[8] The nuclear Hamiltonian of a generic insulating system in the BO approximation is

$$\mathcal{H}_{\mathrm{N}}=\sum_n \frac{1}{2M_n}\left[\boldsymbol{P}_n-\frac{Q_n}{c}\boldsymbol{A}(\boldsymbol{R}_n)-\boldsymbol{\chi}_n\right]^2+U(\{\boldsymbol{R}\}). \qquad (1)$$

The first term is the ion kinetic energy ($\boldsymbol{P}_n=-i\nabla_{\boldsymbol{R}_n}$); the second is the ground state expectation value of the electronic Hamiltonian, including the magnetic field effect on the electronic structure. $\boldsymbol{\chi}_n$ appearing in the first term of Eq. (1) is the so-called geometric vector potential (GVP) or Berry connection, given by[4,5]

$$\boldsymbol{\chi}_n=-i\langle\psi_{\mathrm{el}}(\{\boldsymbol{R}\})|\nabla_{\boldsymbol{R}_n}|\psi_{\mathrm{el}}(\{\boldsymbol{R}\})\rangle, \qquad (2)$$

where $\psi_{\mathrm{el}}(\{\boldsymbol{R}\})$ is, in full generality, the many-body electronic wave function in presence of the field, normalized to the number of electrons: $\langle\psi_{\mathrm{el}}|\psi_{\mathrm{el}}\rangle=N_{\mathrm{el}}$, and depending parametrically on all nuclear coordinates. Whenever this wave function can be chosen real and single valued, the GVP of Eq. (2) vanishes.[4] In a magnetic field, the wave function cannot be made real, and the GVP is nonzero. After integration of the electronic degrees of freedom, a gauge potential associated with the GVP appears in the nuclear Hamiltonian.[4,5,9] This gauge field plays the role of an additional magnetic field, one that couples only to the kinematic degrees of freedom, and not, e.g., to the nuclear moments, which instead experience the real field. We restrict here for simplicity to large gap insulators, where the adiabatic approximation is well justified, and one can safely ignore all excited electronic states in the expression of $\boldsymbol{\chi}_n$. In that case moreover the spin susceptibility is minuscule, and spin effects can also be neglected.

We derive from Eq. (1) the nuclear equations of motion (EOMs) from the Heisenberg time evolution of the positions and velocity operators. Classical equations of motion are then obtained through Eherenfest's theorem

$$M_n\dot{\boldsymbol{V}}_n = -\nabla_{\boldsymbol{R}_n}U + (Q_n/c)\boldsymbol{V}_n \times \boldsymbol{B} + \sum_m \boldsymbol{V}_m \times \boldsymbol{\Omega}^{(nm)}. \quad (3)$$

Equation (3) resembles that of a charged ion in a field, but for the last term, which is precisely the electronic Lorentz force. The gauge invariant quantity $\boldsymbol{\Omega}^{(nm)}$ is the Berry curvature which plays the role of an effective magnetic field (gauge field) in the $3N$-dimensional space spanned by the ionic degrees of freedom ($N$ is the number of nuclei). It is given by

$$\boldsymbol{\Omega}^{(nm)} = -2\,\mathrm{Im}\langle\nabla_{\boldsymbol{R}_n}\psi_{\mathrm{el}}| \times |\nabla_{\boldsymbol{R}_m}\psi_{\mathrm{el}}\rangle \quad (4)$$

and has the dimensions of a magnetic field, in fact proportional to the external field $(B/c)$ when sufficiently weak. Unsurprisingly, the force on ion $n$ now depends upon the velocity of all other ions $m$ through the off-diagonal terms in Eq. (4). If the electrons were infinitely tightly bound to the nuclei (or equivalently, in the limit of large separation between the ions), these off-diagonal terms would vanish. In that regime, $\psi_{\mathrm{el}}$ collapses to a sum of products of single particle orbitals centered around the nuclei. Each is rapidly decaying in space, and each is dragged rigidly along by its nucleus as it moves, thus providing total magnetic screening for every ion. Reality is of course very far from that limit, magnetic screening is only partial, and must be calculated explicitly.

The basic ingredient for computing the Berry curvature, Eq. (4), is the derivative of the electronic wave function with respect to atom position $\boldsymbol{R}_n$. That can be obtained in a electronic structure calculation by finite differencing the electronic wave function $\psi_{\mathrm{el}}$ for two atomic configurations, compensating the arbitrary phase of the wave functions (covariant derivative). Alternatively, $|\nabla_{\boldsymbol{R}_n}\psi_{\mathrm{el}}\rangle$ can be obtained by linear response to an atom displacement.

In order to provide a first exemplification of the electronic Lorentz forces, with a direct analytical and quantitative insight into the properties of the Berry curvature, Eq. (4), we consider here as a simple example the classical dynamics of a neutral homonuclear diatomic molecule in a field. If we set the molecule in motion and freeze the vibrational and rotational degrees of freedom ($\boldsymbol{V}_1 = \boldsymbol{V}_2 \equiv \boldsymbol{V}$), the EOMs are

$$M\dot{\boldsymbol{V}} = (Q/c)\boldsymbol{V} \times \boldsymbol{B} + \boldsymbol{V} \times (\boldsymbol{\Omega}^{(11)} + \boldsymbol{\Omega}^{(12)}) \quad (5)$$

(inversion symmetry requires $\boldsymbol{\Omega}^{(11)} = \boldsymbol{\Omega}^{(22)}$ and $\boldsymbol{\Omega}^{(12)} = \boldsymbol{\Omega}^{(21)}$). Since the molecule is neutral, the total Lorentz force must vanish and $\boldsymbol{\Omega}^{(11)} + \boldsymbol{\Omega}^{(12)} = -Q(\boldsymbol{B}/c)$ must screen completely the nuclear charge $Q$. In the heteronuclear diatomic case, the nuclei are not screened individually, but only globally, in the form $\Sigma_{nm}\boldsymbol{\Omega}^{(nm)} = -(\boldsymbol{B}/c)\Sigma_n Q_n$.[10] If we consider a rigid rotation of the frozen molecule, then $\boldsymbol{V}_1 = -\boldsymbol{V}_2 \equiv \boldsymbol{V}$ around the center of mass and the EOM is

$$M\dot{\boldsymbol{V}} = (Q/c)\boldsymbol{V} \times \boldsymbol{B} + \boldsymbol{V} \times (\boldsymbol{\Omega}^{(11)} - \boldsymbol{\Omega}^{(12)}). \quad (6)$$

The electronic screening field $\boldsymbol{\Omega}_{\mathbf{r}} \equiv \boldsymbol{\Omega}^{(11)} - \boldsymbol{\Omega}^{(12)}$ depends upon the internuclear distance and is related to the electronic Berry phase $\gamma$ accumulated on a single period of rotation,

$$\gamma \equiv \oint_{\partial C(R)} \boldsymbol{\chi}(R) \cdot d\boldsymbol{R} = \int\int_{C(R)} \boldsymbol{\Omega}_{\mathbf{r}}(R) \cdot \hat{\boldsymbol{n}}\,dS, \quad (7)$$

where $C(R)$ is a circle of diameter $R$, $R$ being the interatomic distance. As shown in Ref. 11, $\gamma$ is the electronic contribution to the rotation-induced magnetic moment.

We now wish to address the generically rotating, translating, and vibrating molecule. In general, that calculation can be done by first principle implementation of Eqs. (3) and (4). In order to make the illustration more explicit while keeping it simple, we will focus on a hydrogen molecule, where we can obtain essentially analytical results by describing the electronic structure through Slater's variational linear combination of atomic orbitals (LCAO) approximation based on two $1s$ orbitals.[12] To include the field, we form linear combination of gauge-including atomic orbitals (GIAO)

$$\psi_{\mathrm{el}} = c_1\tilde{\varphi}_1(\boldsymbol{r} - \boldsymbol{R}_1) + c_2\tilde{\varphi}_2(\boldsymbol{r} - \boldsymbol{R}_2),$$

$$\tilde{\varphi}_n = \exp[-(ie)/c\Phi(\boldsymbol{R}_n \to \boldsymbol{r})]\varphi_{1s}(\boldsymbol{r} - \boldsymbol{R}_n), \quad (8)$$

where the phase factor $\Phi(\boldsymbol{r} \to \boldsymbol{r}')$ is the integral of the vector potential along the line connecting the points $\boldsymbol{r}$ and $\boldsymbol{r}'$.[13] $\varphi_{1s}$ is the hydrogenic $1s$ radial wave function for a nuclear charge $\alpha$, taken as variational parameter,[12] $\varphi_{1s}(\boldsymbol{r}) = (\alpha^3/\pi)^{1/2}e^{-\alpha r}$. For a fixed value of the internuclear separation, $\alpha$ minimizes the sum of the electronic energy plus the nuclear-nuclear Coulomb repulsion, and varies from 1 in the limit of large separation to ~2 in the limit of small separation where the $H_2$ molecule collapses to a He atom. We neglect the electron spin due to the large gap between the singlet and triplet (~10 eV). Owing to its simplicity, this trial wave function gives for $H_2$ a crude equilibrium distance of 1.00 Å (experimental 0.74 Å) and a barely reasonable dissociation energy of 4.235 eV (experimental 4.476 eV). However, it illustrates the electronic Lorentz forces very well. At weak field, the one electron matrix elements are

$$\tilde{H}_{nm} = H_{nm}\exp[-(ie/c)\Phi(\boldsymbol{R}_m \to \boldsymbol{R}_n)],$$

$$\tilde{S}_{nm} = S_{nm}\exp[-(ie/c)\Phi(\boldsymbol{R}_m \to \boldsymbol{R}_n)], \quad (9)$$

where $H_{nm} = \langle\varphi_n|H^0|\varphi_m\rangle$ and $S_{nm} = \langle\varphi_n|\varphi_m\rangle$ are the field-free matrix elements.

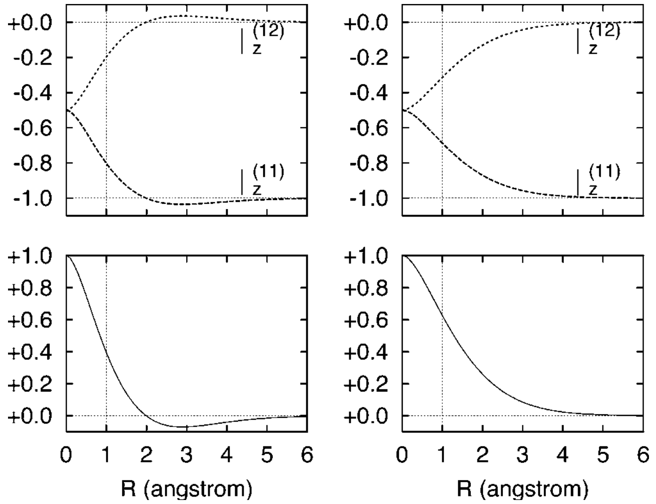

FIG. 1. Top: $\Omega_z^{(11)}$ (solid line) and $\Omega_z^{(12)}$ (dashed line) in units of $(B/c)$ as a function of the interatomic distance, for the $H_2$ molecule. Bottom: The effective magnetic field felt by each proton $1+\mathbf{\Omega_r}$, in units of $(B/c)$. Left-hand panels, field normal to the molecule axis; right-hand panels, field parallel to the molecular axis. The vertical line indicates the theoretical equilibrium distance.

We computed $\mathbf{\Omega}^{(11)}$ and $\mathbf{\Omega}^{(12)}$ with the trial wave function of Eq. (8), directly from Eq. (4). The resulting expression, analytic, contains a number of terms and is too long to be shown here. Since GIAOs give the first-order correction in $(B/c)$ to the zero-field wave functions, we retain only the linear $(B/c)$ term in the $\mathbf{\Omega}$'s, where the zero-order term is zero. These quantities depend on the interatomic distance and on the angle between the molecule axis and the magnetic field, preserving the cylindrical symmetry of the system, independent of the gauge. In the following $\mathbf{\Omega}^{(nm)}$ will indicate the coefficient of the first-order term in $(B/c)$.

The upper panels of Fig. 1 show $\mathbf{\Omega}^{(11)}$ and $\mathbf{\Omega}^{(12)}$ as a function of the interatomic distance, for two relative orientations of the molecule with respect to the magnetic field, which we choose parallel to the $z$ axis. For large interatomic separation $R$, i.e., in the dissociation limit, the off-diagonal $\mathbf{\Omega}^{(12)}$ vanishes and $\mathbf{\Omega}^{(11)}$ reaches the asymptotic value $-1$. This reflects the fact that the motion of the two protons is decoupled in the dissociation limit and the electronic screening of the individual nuclei is complete. For small interatomic separation, both $\mathbf{\Omega}^{(11)}$ and $\mathbf{\Omega}^{(12)}$ (and by symmetry $\mathbf{\Omega}^{(22)}$ and $\mathbf{\Omega}^{(21)}$) tend to $-1/2$, recovering the correct screening of an isolated He atom. For arbitrary interatomic distance, the sum of $\mathbf{\Omega}^{(11)}$ and $\mathbf{\Omega}^{(12)}$ is identically $-1$, which fulfills Eq. (5) and warrants total screening of the center-of-mass motion. The lower panels of Fig. 1 show the effective relative magnetic field at the proton site, $(1+\mathbf{\Omega_r})$ as a function of the interatomic distance, for two orientations of the molecule relative to the field. At the equilibrium distance of $R \simeq 1$ Å, the proton's Lorentz force is that of a reduced effective charge ranging beetween $+0.4|e|$ and $+0.6|e|$, depending on orientation. (The true reduction is actually weaker, since our variational wave function slightly overestimates the electronic screening.) The approximate rotational $g$-factor[14] computed by Eq. (7) in the present approximation is 0.62, in fair agreement with experiment,[14] and with more accurate calculations,[11] yielding 0.88. This sort of error does not impair the value of the present approximation as an analytical illustration of the method.

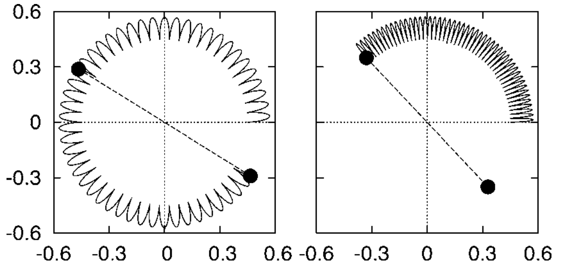

FIG. 2. Simulated trajectories of the $H_2$, in the presence of a magnetic field. Left-hand panel: neglecting the Berry curvature term. Right-hand panel: with the Berry curvature term. In both cases, the molecule was set initially parallel to the $x$ axis and the bond compressed 0.1 Å. The molecule rotates in the counterclockwise sense. For a field 10 T, the estimated rotation period is of $2 \times 10^{-5}$ s. The units of the plots are Å.

Armed with the Berry curvatures $\mathbf{\Omega}^{(nm)}$—now known analytically—and with a simple parametrization of the interatomic potential $U(R)$, we can describe the classical dynamics of $H_2$ in a field. As in a first principles molecular dynamics simulation, we integrate the equation of motion, Eq. (3), for the $H_2$ molecule, exploring the effect of different initial (Cauchy) conditions.[15] By way of example, we start by compressing or stretching the molecular bond and let it be free to vibrate and/or rotate. The restoring force sets the two protons in motion initially in the radial direction but soon their trajectory is deflected by the Lorentz forces. If the molecule initially lies in the plane perpendicular to the magnetic field, the resulting orbits resemble cycloids in that plane. The resulting trajectories are shown in Fig. 2. The sense of rotation is determined by the initial condition of stretching or compression.

To clarify the effect of the electronic Lorentz forces on the EOM we show in the left-hand panel of Fig. 2 the same trajectories now obtained by neglecting the Berry curvatures from Eq. (3)—i.e., only retaining the bare Lorentz force $(Q/c)\boldsymbol{V}\times\boldsymbol{B}$. When the Berry curvature is included, the angular velocity of the cycloid is reduced by the screening action of the electrons by a factor $\sim 0.4$, which is also the average fraction of magnetic field felt by the ions during the vibrations around the equilibrium position (see $\mathbf{\Omega_r}$ in Fig. 1). We note that this reduction factor measures the strength of the effective magnetic field at the proton site, and differs from the rotational $g$-factor (here 0.62), which measures instead its integral over the orbit spanned in a full rotation. Summing up, implementation of Eqs. (3) and (4) yields a description of nuclear motion whose accuracy is only limited by that of the underlying electronic calculation.

All of the above is classical nuclear motion. In the quantum EOMs for the nuclei, the presence of the GVP of Eq. (2) must be considered. In particular, starting from the zero-field nuclear Hamiltonian of a diatomic molecule, we may explore how the GVP term of Eq. (2) influences the rotovibrational spectrum. In the symmetric gauge, $\boldsymbol{A}(\boldsymbol{x})=(1/2)\boldsymbol{B}\times\boldsymbol{x}$ one can separate center of mass and relative distance in Eq. (1). The distance Hamiltonian is $\mathcal{H}_\mathrm{R}=1/(2\mu)\ [\boldsymbol{p}_R+(e/c)\boldsymbol{A}(\boldsymbol{R})+\boldsymbol{\chi}_R]^2+U(R)$ where $\boldsymbol{\chi}_R=(e/2c)\boldsymbol{B}\times\boldsymbol{R}(S-1)/(S+1)$, $S$ being the overlap integral between the two atomic orbitals. The curl of $\boldsymbol{\chi}_R$ is $\boldsymbol{\Omega}_\mathbf{r}$. For ordinary laboratory magnetic field intensities, the field can be considered as a perturbation, therefore we expand the Hamiltionian up to first order in the field $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$. $\mathcal{H}_0$ is the unperturbed Hamiltonian of a harmonic vibrating rotator, $\mathcal{H}_1=(eB)/(2\mu c)L_z 2S/(S+1)$ is the rotational paramagnetic term. The basis of the unperturbed Hamiltonian $\mathcal{H}_0$ can be labeled by the quantum numbers $(n,l,m)$, and the spectrum is given by the rotovibrational levels of the diatomic molecule. To first order in $(B/c)$, $\mathcal{H}_1$ removes the degeneracy of the rotational levels according to the usual Zeeman splitting $E_{nlm}=E^{(0)}_{nlm}+g_R\mu_\mathrm{nuc}Bm$, where $g_R$ is the rotational $g$-factor. The eigenstates have corrections of order $(B/c)$ due to the term $S/(S+1)$, which mixes an unperturbed state with other states with the same $(l,m)$ and different $n$. However, for a field of 1 T, the coupling between vibrational states is of the order of $10^{-5}$ cm$^{-1}$, much smaller than the centrifugal and anharmonic couplings, which are of the order of 10 cm$^{-1}$. To second order in $(B/c)$, there will be diamagnetic shifts affecting mainly the states with $L_z=0$. Despite the rotation, the canonical angular momentum $L_z$ is a conserved quantity. In the symmetric gauge, the mechanical angular momentum is

$$I\omega = L_z + \frac{eB}{2c}\frac{2S}{S+1}R^2, \tag{10}$$

where $I$ and $\omega$ are, respectively, the momentum of inertia and the angular velocity. The second term on the right-hand side is always positive, depends on the vibrational state of the molecule, and is of the order of $(B/c)$. The physical rotation of the molecule correspond to the expectation value of $I\omega$; when $m\neq 0$ the difference between $I\omega$ and $L_z$ is negligible because it is of order $(B/c)$. However, Eq. (10) shows that even when $L_z=0$, a small amount of rotation still exists.

In conclusion, we presented a convenient formalism to calculate the all important electronic contribution to adiabatic Lorentz forces for atomistic dynamics in a magnetic field, based on Berry connections and ideally suitable for future *ab initio* simulations. We demonstrated its validity and applicability in the simple example of $H_2$ where variational wave functions provide approximate but analytical results for the the Berry connection and Berry curvatures. The example demonstrates a weak field induced coupling between rotations and vibrations.

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[6] The electric field experienced by a molecule moving in a uniform magnetic field is $\boldsymbol{\mathcal{E}}=\boldsymbol{V}_\mathrm{CM}\times\boldsymbol{B}$, where $\boldsymbol{V}_\mathrm{CM}$ is the center-of-mass velocity. For gaseous hydrogen at 1000 K, the mean quadratic speed is $\sim$4500 m/s. Thus $\mathcal{E}=4.5\times10^{-7}$ V/Å for a magnetic field of 1 T.

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[15] We integrated the EOMs by an adaptive time step fourth-order Runge-Kutta scheme. Velocity Verlet and predictor-corrector lead to an irreversible energy transfer between vibrational and rotational degrees of freedom.