Magnons in real materials from density-functional theory

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Over the last 30 years, Density-Functional Theory (DFT) $^1$ has brought a large number of properties of real materials within the predictive range of first-principles calculations. Even though excited states cannot be properly described within DFT—which strictly speaking only applies to the electronic ground states—the use of the adiabatic approximation allows to predict the vibrational excitation spectra of semiconductors $^2$ and metals $^3$ to a very high accuracy. Magnetic excitations are also adiabatically decoupled from charge excitations. However, the adiabatic decoupling of spin excitations has only been implemented so far using ad-hoc models—such as the Heisenberg Hamiltonian $^4$—which are difficult to reconcile with an itinerant picture of magnetism. A substantial step toward the calculation of magnetic excitations within a firm theoretical framework has been done by Niu and Kleinman (NK) $^5$ who showed how a generalization of the Born-Oppenheimer (BO) method can be used to rigorously, although approximately, decouple spin and charge excitations of a many-electron system. The NK method lends itself quite naturally to be implemented within DFT. The latter requires a proper description of non-collinear magnetic structures, a task which has hardly been tackled so far in full generality. Although the local spin-density approximation (LSDA) was formulated long ago so as to account for general magnetic structures $^6$, the vast majority of the LSDA calculations assumes that the magnetization is aligned to a same direction all over the system. Most of the existing applications to non-collinear structures rely on some sort of atomic-sphere approximation (ASA) in which different spin quantization axes are chosen within different spheres $^7$. Progresses beyond this rather crude approximation have been made only recently $^8$. $^9$.

In the present work we combine the adiabatic decoupling method of Ref. $^3$ with a newly developed constrained DFT scheme which allows the calculation of the spin-spiral states necessary to implement the NK spin-wave equations of motion, without using any atomic-sphere approximation. Our implementation—which is based on the plane-wave pseudo-potential method—is successfully demonstrated by calculating the magnon dispersions of iron. This paper is organized as follows: we first briefly review and generalize the NK adiabatic decoupling scheme; we then introduce our constrained DFT approach to spin-spiral states, and we finally present our results for iron.

In order to establish an adiabatic decoupling scheme that allows to derive from first principles the spin-fluctuation equations of motion, we first derive the classical equations of motion for nuclei in a molecule or in a solid by using of the concept of adiabatic coherent state. This procedure has the advantage of not making explicit reference to the smallness of the nuclear kinetic energy term in the Hamiltonian. Because of this, we can then make the ansatz that a similar method applies in the general case where no such small term exists in the Hamiltonian, but the density of states of the system is still characterized by a low-lying portion which is well separated in energy from the rest. This procedure provides thus an unified approach to the classical BO approximation and to the NK method.

Let us consider a system of interacting electrons (of mass $m = 1$) and nuclei (of mass $M \gg m$ and in number $N$), and let us indicate by capital letters the coordinates and momenta of the nuclei, ($R$, $P$), and by lower-case letters those of the electrons, ($r$, $p$). The Hamiltonian of the system reads:

\[ H = \frac{1}{2M}P^2 + \frac{1}{2}p^2 + V(r, R) \] (1)

(here and in the following quantum operators are indicated by boldfaces). Let us now consider the wavefunction $\Psi_{R, P}(r, R)$ which minimizes the expectation value of the Hamiltonian, Eq. (1), with the constraint that the expectation values of $R$ and $P$ equal $\mathcal{R}$ and $\mathcal{P}$, respectively. By introducing the $\lambda$ and $\mu$ Lagrange multipliers for the constraints on $R$ and $P$ respectively, $\Psi_{R, P}$ can be formally obtained as the ground-state solution of the eigenvalue equation:

\[ [H - \lambda(\mathcal{R} - R) - \mu(\mathcal{P} - P)]\Psi_{R, P} = \epsilon(\mathcal{R}, \mathcal{P})\Psi_{R, P}, \] (2)
where \( \lambda \equiv \lambda(R, P) \) and \( \mu \equiv \mu(R, P) \) are chosen in such a way that: \( \langle \Psi_{R, P} | H | \Psi_{R, P} \rangle = R \) and \( \langle \Psi_{R, P} | \partial | \Psi_{R, P} \rangle = P \). It is easy to verify that when \( H \) is the Hamiltonian of a harmonic oscillator, \( H = \frac{1}{2M} P^2 + \frac{1}{2} k R^2 \), the eigenvalue equation, Eq. (2), yields directly Glauber’s canonical coherent states \([1]\). For this reason, in the general case we name \( \Psi_{R, P}(r, R) \) an adiabatic coherent state (ACS) \([2]\) and we refer to \((R, P)\) as to the label of the ACS.

Let us suppose that the time evolution of an ACS is an ACS: this is true for harmonic oscillators and canonical coherent states, but in general this is only an approximation. The low energy dynamical properties of the system are then given by the variational problem:

\[
\delta \int_{t_0}^{t_1} \left( \Psi_{R(t), P(t)} \right) \left( i \frac{\partial}{\partial t} - H \right) \Psi_{R(t), P(t)} \, dt = 0, \quad (3)
\]

which, following the NK procedure, leads the equations of motion for the \((R, P)\) label:

\[
\left( \begin{array}{c}
\Omega^R_{R, R} & \Omega^R_{P, R} \\
\Omega^P_{R, P} & \Omega^P_{P, P}
\end{array} \right) \left( \begin{array}{c} R \\
\dot{R}
\end{array} \right) = \left( \begin{array}{c}
\frac{\partial \Omega^R_{P, R}}{\partial P} \frac{\partial \Psi_{R, P}}{\partial P} \\
\frac{\partial \Omega^P_{P, P}}{\partial P}
\end{array} \right), \quad (4)
\]

where the \( \Omega \)'s are matrices defined as \( \Omega_{i,j} = -2 \text{Im} \left( \frac{\partial \Psi_{R, P}}{\partial x_i} \frac{\partial \Psi_{R, P}}{\partial x_j} \right) \), and the \( i \) or \( j \) subscripts indicate the components of the \( R \) and \( P \) \( 3N \)-dimensional vectors. From this definition, it follows that \( \Omega^R_{i,j} = -\Omega^R_{j,i} \). Following the literature \([3, 13]\), we name the \( \Omega \) matrices the Berry curvature of the ACS. In order to recover the classical equations of motion for the nuclear degrees of freedom, we first simplify the eigenvalue equation \((2)\) using the fact that \( H \) is quadratic in \( P \). Taking into account that \( [P, e^{\partial P R}] = P e^{\partial P R} \), a simple algebraic manipulation in Eq. \((2)\) allows to cast \( \Psi_{R, P} \) and \( \epsilon(R, P) \) into the form:

\[
\Psi_{R, P}(r, R) = e^{\partial P R} \Phi(R, R), \quad (5)
\]

\[
\epsilon(R, P) = \frac{1}{2M} P^2 + \epsilon(R), \quad (6)
\]

where the real wave-function \( \Phi \) satisfies the eigenvalue equation:

\[
[H - \lambda(R - R)] \Phi_R = \epsilon(R) \Phi_R, \quad (7)
\]

and the Lagrange multiplier \( \lambda \equiv \lambda(R) \) is chosen in such a way that: \( \langle \Phi_R | H | \Phi_R \rangle = R \). Using Eq. \((1)\) and the reality of \( \Phi_R \), the \( \Omega \)'s can be explicitly calculated: \( \Omega^R_{i,j} = -2 \text{Im} \left( \frac{\partial \Phi_R}{\partial x_i} \frac{\partial \Phi_R}{\partial x_j} \right) \), and \( \Omega^P_{i,j} = \Omega^R_{j,i} = 0 \). By inserting these \( \Omega \)'s and the expression given by Eq. \((5)\) for \( \epsilon(R, P) \) into Eq. \((6)\), one finally arrives at a set of Hamilton-like equations for the nuclear motion. In order identify \( \epsilon(R) \) with the familiar BO energy surface, it is enough to neglect in Eq. \((5)\) the nuclear kinetic-energy term present in \( H \) \((1/M \approx 0)\). It is important to remark that—while the smallness of \( 1/M \) is the physical reason why nuclear vibrations are adiabatically decoupled from electronic excitations—this property has not been formally used to establish the classical equations of motion, but only to identify \( \epsilon(R) \) with the traditional BO energy surface. In principle, \( \epsilon(R) \) could be as well calculated from its definition, Eq. \((6)\), without letting \( 1/M \) go to \( 0 \). When studying the electronic spectrum of magnetic systems, no such small term exists in the Hamiltonian. Nevertheless, spin excitations can be adiabatically decoupled from charge excitations by using the magnetic BO surface obtained from the magnetic analog of Eq. \((7)\).

Spin excitations are characterized by the fluctuation of the spin polarization, \( \bar{M}(\vec{r}) \), much in the same way as nuclear vibrations are characterized by the fluctuation of the nuclear canonical coordinates, \((R, P)\). In both cases, the fluctuating observable can be identified with the label of an appropriate ACS. Magnetic ACS (MACS) are thus labeled by a vector field \( \bar{M}(\vec{r}) \), \( \Psi_{[\lambda]} \), and they are solution of the variational problem:

\[
E[\bar{M}] = \min (\Psi | H | \Psi), \quad (8)
\]

with the constraint:

\[
(\Psi | \psi(r) + \delta \psi(r) | \Psi) = \bar{M} \psi(r), \quad (9)
\]

where \( H \) is the many-body Hamiltonian of the system, the \( \psi \)'s are fermion spinor field operators, and \( \delta \equiv (\sigma_x, \sigma_y, \sigma_z) \) the Pauli matrices.

Following NK, the linearized equations of motion for \( \bar{M} \equiv \bar{M}(\vec{r}, t) \) read \((h = 1)\):

\[
\sum_{\beta} \int d^3r'' '' \Omega_{\alpha \beta}(\vec{r}', \vec{r}'') \bar{M}_{\beta}(\vec{r}'', t) = \sum_{\beta} \int d^3r'' '' K_{\alpha \beta}(\vec{r}', \vec{r}'') \bar{M}_{\beta}(\vec{r}'', t), \quad (10)
\]

where \( \Omega \) is the Berry curvature of the MACS and \( K \) the matrix of the second derivatives of its energy with respect to its label, \( \bar{M} \):

\[
\Omega_{\alpha \beta}(\vec{r}', \vec{r}'') = -2 \text{Im} \left( \frac{\delta \Psi_{[\lambda]} \bar{M}_{\alpha}(\vec{r}', \vec{r}'')}{\delta \Psi_{[\lambda]} \bar{M}_{\beta}(\vec{r}', \vec{r}'')} \right), \quad (11)
\]

\[
K_{\alpha \beta}(\vec{r}', \vec{r}'') = \frac{\delta^2 E[\bar{M}]}{\delta \bar{M}_{\alpha}(\vec{r}') \delta \bar{M}_{\beta}(\vec{r}'')}, \quad (12)
\]

In order to calculate the Berry curvature, we use a finite-difference approach \([3, 14]\). To keep the notation as simple as possible, we define \( \Psi_0 \equiv \Psi[M_{\alpha}(\vec{r}')], \Psi_1 \equiv \Psi[M_{\alpha}(\vec{r}')] + \epsilon \delta_{\alpha \beta} \delta(\vec{r}' - \vec{r}''), \) and \( \Psi_2 \equiv \Psi[M_{\alpha}(\vec{r}') + \epsilon \delta_{\alpha \beta} \delta(\vec{r}' - \vec{r}'')] \). We have then: \( \Omega_{\alpha \beta}(\vec{r}', \vec{r}'') \approx -\frac{\epsilon}{2} \text{Im} \left( \Psi_1 | \Psi_0 \right) \Psi_2 - \Psi_0 - \frac{\epsilon}{2} \text{Im} \left( \Psi_1 | \Psi_2 \right) + \left( \Psi_2 | \Psi_0 \right) + \left( \Psi_0 | \Psi_1 \right) \). By using the relation: \( \langle \Psi_1 | \Psi_2 \rangle \approx \log \langle \Psi_1 | \Psi_2 \rangle + 1 \), we finally arrive at the relation: \( \Omega_{\alpha \beta}(\vec{r}', \vec{r}'') = -\text{Im} \log \left( \langle \Psi_0 | \Psi_1 \rangle \langle \Psi_1 | \Psi_2 \rangle \langle \Psi_2 | \Psi_0 \rangle \right) \).

Before proceeding further, we transform the constrained variational problem, Eqs. \((10)\), into a non-constrained one by making use of a penalty functional,
\[ P[\Psi], \text{ which favors those states whose magnetization, } \vec{M}(\vec{r}) = (\Psi | \vec{M} \Psi) = A \int (\vec{M}(\vec{r}) - \vec{M}(\vec{r}))^2 d^3r. \] 

In the limit where \( A \to +\infty \), the state which minimizes the functional: 
\[ E[\vec{M}, \Psi] = (\Psi | \vec{H} | \Psi) + A \int (\vec{M}(\vec{r}) - \vec{M}(\vec{r}))^2 d^3r \] 
without any constraints but the trivial one on state normalization, will solve the variational problem, Eq. (8), with the constraint given by Eq. (9). Variation with respect to \( \Psi^* \) leads to the eigenvalue equation:

\[ H\Psi + 2A \sum_i \vec{\sigma}_i \cdot (\vec{M}(\vec{r}_i) - \vec{M}(\vec{r}_i))\Psi = E_A[\vec{M}]\Psi, \quad (13) \]

where the sum runs over electrons.

Eq. (13) is formally equivalent to a many-body Schrödinger equation where, in addition to physical interactions, electrons are subject to an external magnetic field whose magnitude, \( \vec{B}(\vec{r}) = 2A (\vec{M}(\vec{r}) - \vec{M}(\vec{r})) \)
depends self-consistently upon the solution of the equation, \( \Psi \). When \( A \) grows large, \( \vec{B} \) has the effect to make \( \vec{M}(\vec{r}) \) closer and closer to \( \vec{M}(\vec{r}) \), so that \( \vec{B}(\vec{r}) \to 2A(\vec{M}(\vec{r}) - \vec{M}(\vec{r})) \) tends to a finite limit, and the value of the penalty functional tends to zero. We conclude that in the large-\( A \) limit the ground-state energy of the Schrödinger equation, Eq. (13), gives the value of the constrained minimum, Eqs. (8-9): 
\[ \lim_{A \to +\infty} E_A[\vec{M}] = E[\vec{M}] \]

An approximate solution of Eq. (13) can be found using DFT within the LSDA, provided that the latter is formulated in such a way as to allow for arbitrary, non collinear, magnetic structures. In the LSDA, the many-body Hamiltonian appearing in Eq. (13) is replaced with an independent-electron Hamiltonian where the effective one-body potential depends self-consistently upon the electron charge density and spin polarization. The implementation of the constraining penalty function in a non-collinear LSDA code thus requires a trivial modification of the dependence of the self-consistent potential upon the spin polarization.

Inspection of the microscopic distribution of the magnetization resulting from various LSDA calculations shows that it is non-vanishing mostly in the neighborhood of atoms (or molecules, in magnetic molecular crystals), and that within these neighborhoods its direction remains almost constant even when different atomic (molecular) moments are not aligned. At variance with the assumptions which underlie the ASA treatment of (non-collinear) magnetism, small deviations from perfect alignment may occur even within an atomic (or molecular) volume, and this quasi-collinearity results from the contribution of many occupied Kohn-Sham orbitals whose individual magnetization is far from collinear. In view of this fact, we choose to label the MACS with atomic (or molecular) moments, rather than with a continuous magnetization. This discretization introduces a natural coarse graining in the treatment of the excitation spectrum, by cutting away all the fluctuations whose wavelength is shorter than the inter-atomic (\( \omega \)) distance, and whose high-energies would be incompatible with the adiabatic decoupling scheme adopted here.

Atomic magnetic moments are defined through the relation: 
\[ \vec{m}(\vec{R}) = \int d^3r \omega(\vec{r} - \vec{R}) \vec{M}(\vec{r}), \]
where the \( \vec{R} \)'s indicate atomic positions, and \( \omega(\vec{r}) \) is a weight function which is equal to one in a region around the origin and zero elsewhere. In our applications, we choose these regions to be the largest possible non-overlapping spheres. Within this picture, long-wavelength magnetic excitations can be thought as time-dependent deviations of the localized moments from their ground-state configuration. Analogously to the current terminology adopted for vibrational excitations, a pattern of atomic moments, \( \{ \vec{m}(\vec{R}) \} \) is called a frozen magnon, and the corresponding matrix of \( \omega(\vec{r}) \) is called a pseudo-potential method [18]. Plane waves up to a limit where the ground-state energy of the solution of the equation, \( \Psi \), with the constraint given by Eq. (9).
the basis set, while Brillouin-zone integrations were performed on a $8 \times 8 \times 8$ mesh, with a Gaussian-smearing of 0.03 Ry \[19\]. In Fig. 1 we display the results of our calculations, performed for $\mathbf{q}$ along the (100) direction, while the ground-state magnetization axis was chosen to be (001). The agreement with available experiments is very good, thus giving confidence in the general theoretical framework followed in this work.

We believe that the adiabatic decoupling scheme by Niu and Kleinman, based on the concept of adiabatic coherent state, still needs stronger theoretical foundations. However, we have demonstrated that this scheme naturally leads to the well established Born-Oppenheimer classical equation of motion for nuclei in molecules or solids. Furthermore, this scheme can be straightforwardly implemented within density-functional theory and, when applied to magnetic excitations of bcc iron, it leads to magnon dispersions in excellent agreement with experiment. We conclude that further theoretical and computational work will probably demonstrate the effectiveness of this method to deal with slow dynamics in quantum systems.

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FIG. 1. Calculated and experimental magnon dispersions in iron. Open hexagons: pure iron at 10K [20]. Open triangles: Fe with 12 % Si) at room temperature [21]. Full hexagons: this work. The line is a guide for the eye.