

## Ground States of Constrained Systems: Application to Cerium Impurities

P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai<sup>(a)</sup>

*Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany*

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We present an extension of the density-functional theory to the lowest states compatible with arbitrary constraints. A broad class of interesting excitation problems connected with charge and magnetization fluctuations can be treated by such a method. We demonstrate the usefulness in *ab initio* calculations for Ce impurities.

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In recent years there have been several efforts to generalize density-functional theory (see, e.g., Lundqvist and March<sup>1</sup>). Of special interest to us is the work of Gunnarsson and Lundqvist<sup>2</sup> who showed that in addition to the true ground state also the lowest states for each symmetry can be calculated. In this note we want to generalize this approach and show that by using more general constraints interesting problems connected with charge and magnetization fluctuations in solids can be treated. We will demonstrate the usefulness of this approach in model calculations for Ce impurities in metals.

As a first example of a more general constraint we examine charge fluctuations within a certain volume  $V$  in the solid. Especially we are interested in the lowest energy  $E(N)$  compatible with the constraint that the volume  $V$  contains exactly  $N$  electrons. This energy may be interpreted as the ground state of the constrained system. If one takes the constraint into account by a Lagrange parameter  $v$ , the lowest energy  $E(N)$  is given by

$$E(N) = \min[E\{n(\vec{r})\} + v\{\int_V d^3r n(\vec{r}) - N\}], \quad (1)$$

where  $E\{n(\vec{r})\}$  is the usual functional, the absolute minimum of which represents the ground-state energy. By minimizing (1) with respect to  $n(\vec{r})$  we obtain in the Kohn-Sham equations an additional potential  $v$ , being constant within the volume  $V$  and zero otherwise. The well depth  $v$  has to be adjusted such that the resulting charge density  $n_v(\vec{r})$  gives exactly  $N$  electrons within the volume  $V$ . Instead of calculating  $E(N)$  from  $E\{n_v(\vec{r})\}$  we can also calculate directly the energy difference with respect to a reference state  $N_0$ , e.g., the ground state, by taking advantage of the Hellmann-Feynman theorem

$$\frac{dE(N)}{dN} = -v$$

or  $\Delta E(N) = -\int_{N_0}^N dN' v(N'). \quad (2)$

Thus the knowledge of  $v(N')$  is sufficient to calculate the excitation energy  $\Delta E$ . Physically we can view the potential  $v$  as the "force" necessary to constrain the system to the desired configuration and  $\Delta E$  as the resulting internal "strain energy" of the system. For the ground state  $N_0$  the force  $v$  vanishes, since  $dE/dN=0$ . Moreover, for small deviations  $\Delta N = N - N_0$ , the potential  $v$  will in general be proportional to  $\Delta N$  so that  $\Delta E \sim (\Delta N)^2$ .

The constraint chosen in (1) or (2) can be quite arbitrary. In this context it is interesting to remember Levy's definition<sup>3</sup> of the functional  $E\{n(\vec{r})\}$  as the lowest energy subject to the constraint that the wave function gives the required charge density  $n(\vec{r})$ . Thus we are going only one step down in the minimalization by choosing less restrictive constraints the form of which are defined by the physical problems studied. If for instance for a discrete system we constrain the symmetry of the wave function, we obtain the theorem of Gunnarsson and Lundqvist for the lowest energies for each symmetry. If on the other hand we constrain the population of a certain atomic orbital, we can rederive Janak's formula  $\epsilon_l = \partial E / \partial n_l$ ,<sup>4</sup> or, in the integrated form, Slater's transition state.<sup>5</sup> Thus our method represents a generalization of these ideas to continuous systems.

Of more interest than variation of the total charge  $N$  is the variation of the local  $d$  charge in a single cell of a transition metal or the local  $f$  charge in a rare-earth metal. The appropriate functional is then

$$E(N_f) = \min[E\{n(\vec{r})\} + v_f\{\int_{V_s} d^3r n_f(\vec{r}) - N_f\}]. \quad (3)$$

Here  $n_f(\vec{r})$  is the  $f$ -charge density which should be constrained to a total  $f$  charge of  $N_f$  electrons within the local Wigner-Seitz sphere  $V_s$ . The minimalization leads to a constant projection potential  $v_f$  acting only on the  $l=3$  angular momentum components of the wave function in the considered Wigner-Seitz sphere. Since the constraint affects only the  $f$  charge in the considered cell, the *spd*

electrons in this cell as well as all other electrons in the neighboring cells relax in order to minimize the energy, describing in this way an optimally screened excitation. The corresponding energy difference should be directly connected with the screened Coulomb matrix element  $U$ . For instance, in the atomic limit  $U$  is given by the sum of  $\Delta E$  for the  $N_f + 1$  and  $N_f - 1$  configurations.<sup>6</sup>

Such constrained ground-state calculations should be of special significance for magnetism and magnetic interactions. Because of the work of Hubbard<sup>7</sup> and others<sup>8,9</sup> it is generally assumed that in metallic magnets thermal fluctuations of the local moments vary slowly in time so that the static approximation appears to be a natural starting point. In a recent paper Small and Heine<sup>10</sup> have pointed out how, in the frame of the Hartree-Fock method, ground-state calculations with artificial exchange fields can be effectively used to calculate exchange interaction energies. Here we want only to show that analogous but more realistic calculations can be done within density-functional theory by introducing the corresponding constraints.

For instance, in order to calculate longitudinal fluctuations of the local moment  $M$  in a cell  $V$  one has to calculate

$$E(M) = \min\{E(n(\vec{r}), m(\vec{r})) + H\{\int_V m(\vec{r}) d^3r - M\}\}. \quad (4)$$

Physically  $H$  represents a magnetic field, being constant in the cell  $V$  and vanishing outside of  $V$ . Williams<sup>11</sup> has recently studied such longitudinal fluctuations in Invar systems. His method of introducing two Fermi energies  $E_F^\pm$  for both spin directions is a special case of the above approach if  $V$  is identical with the crystal volume ( $E_F^\pm = E_F \pm H$ ). If also the direction of the moment is changed we have to replace the quantities  $m(\vec{r})$ ,  $M$ , and  $H$  in (4) by vectors. Especially interesting is the case where only the direction  $\hat{m}(\vec{r})$  is fixed whereas the absolute magnitude of the moment is allowed to relax, e.g.,  $\hat{m}(\vec{r}) = \vec{e}$  within the cell  $V$ . However, this constraint leads to problems in more complicated cases when one constrains the directions in various cells to different values  $\vec{e}_1, \vec{e}_2, \dots$ . The magnetization vector  $\vec{m}(\vec{r})$  being a continuous quantity would then vary discontinuously at the cell boundaries. Therefore a less restrictive constraint affecting only the average direction in cell  $V$  should be more appropriate:

$$E(\vec{e}) = \min\{E(n(\vec{r}), \vec{m}(\vec{r})) + \vec{H}\{\int_V d^3r \vec{m}(\vec{r}) - \vec{e}|\int_V \vec{m}(\vec{r}) d^3r|\}\}. \quad (5)$$

In the Kohn-Sham equation one obtains in cell  $V$  an additional field  $\vec{h} = \vec{H} - \vec{e}(\vec{e} \cdot \vec{H})$ , which is orthogonal to  $\vec{e}$  so that  $\vec{H}$  also can be assumed to be perpendicular to  $\vec{e}$  without loss of generality. This is due to the fact that in (5) the energy is already minimized with respect to longitudinal fluctuations. By means of the Hellmann-Feynman theorem the change  $dE$  of the energy due to a directional change  $d\vec{e}$  leads to the classical result  $dE = -\vec{H}(\vec{e})M(\vec{e}) \cdot d\vec{e}$ , where  $M$  is the total local moment. For finite rotations one has to integrate over all intermediate rotation angles.

The generalization to the case of many interacting moments with longitudinal and transversal fluctuations is obvious. In each cell one has to introduce constraining fields  $\vec{H}_1, \dots, \vec{H}_N$  which have to be adjusted in order to fix the local moments to the required values  $\vec{M}_1, \dots, \vec{M}_N$ . The resulting energy  $E(\vec{M}_1, \dots, \vec{M}_N)$ , calculated from  $dE = -\sum_i \vec{H}_i \cdot d\vec{M}_i$ , can be considered as an effective Hamiltonian describing only the contracted degrees of freedom of the local moments. For instance, for small deviations  $\Delta\vec{M}_i = \vec{M}_i - \vec{M}_i^0$  from the ground state the energy will be quadratic in  $\Delta\vec{M}_i$ <sup>9,10</sup>:

$$\Delta E \simeq \frac{1}{2} \sum_{i,j} \vec{J}_{ij} \cdot \Delta\vec{M}_i \Delta\vec{M}_j. \quad (6)$$

The exchange-coupling constants  $J_{ij}$  are related to the constraining fields  $\vec{H}_i$  by  $\vec{H}_i = -\sum_j \vec{J}_{ij} \cdot \Delta\vec{M}_j$ , i.e., the  $\vec{H}$  field of cell  $i$  has to balance the internal exchange fields  $\vec{J}_{ij} \cdot \Delta\vec{M}_j$  arising from the moment changes in the neighboring cells  $j$ .

Another interesting application of our method would be the calculation of the energy difference between two stable magnetic configurations. For instance, for two magnetic impurities in a noble-metal host usually both the ferromagnetic as well as the antiferromagnetic configurations are stable. Both can be continuously transferred into each other by, e.g., the application of a staggered longitudinal field on the ferromagnetic configuration which induces a difference  $\Delta M = M_1 - M_2$  between the two moments. By increasing  $\Delta M$  finally the antiferromagnetic solution is reached. One might as well apply transversal fields of opposite sign on both impurities which would rotate the moments from ferromagnetic to antiferromagnetic alignment.

In all of the above applications the Hellmann-Feynman theorem is proposed to calculate the relevant energy differences. Whereas it is well known that this is problematic for the calculation of real forces, it should be much less so for the above cases. For real forces the anisotropic parts of the charge density in a given cell play a decisive role,

which are not calculated completely self-consistently in a muffin-tin or atomic sphere approximation, whereas in all of the above examples only "isotropic" quantities like the local charges or the local moments are needed, which can be calculated much more reliably. Therefore corrections for non-self-consistency<sup>12</sup> should be small.

In the following we will illustrate the method of constraints in *ab initio* calculations for Ce impurities in metals. The calculations are based on the local density approximation and a muffin-tin description of the atomic potentials. The embedding of the impurity into the host is described by Korringa-Kohn-Rostoker Green's functions which are constructed from a self-consistent host band structure. The potentials of the impurity and the neighboring host atoms are then calculated self-consistently. For details about the method we refer to Podloucky *et al.*<sup>13</sup> and Braspenning *et al.*<sup>13</sup> First we want to study the change  $\Delta E(N_f)$  of the energy by changing the  $f$  occupation  $N_f$  of the Ce impurity. A semirelativistic calculation yields  $N_f^0 = 1.18$  for Ce impurities in Pd and 1.25 for Ce in Ag. The  $f$  occupation in the impurity cell is then changed by a Lagrange potential  $\nu_f$  as in (3). Figure 1(a) shows the dependence of  $\nu_f$  on  $\Delta N_f$  as determined self-consistently. We obtain a nearly linear dependence which upon integration then yields an almost quadratic dependence of the energy change  $\Delta E$  on  $\Delta N_f$ . If the Coulomb interaction  $U$  is estimated from  $U = \Delta E(N_f^0 + 1) + E(N_f^0 - 1)$ , we obtain values of 6.6 eV for Ce in Ag and 8.1 eV for Ce in Pd. These values should be compared with experimental estimates of 6 eV for elemental Ce,<sup>14</sup> and with a value of 5 eV from renormalized atomic calculations.<sup>6</sup>

The second example is connected with changing the form of the  $f$  wave function of Ce. Schlüter and Varma<sup>15</sup> have proposed a bistability model for Ce based on a simplified calculation which suggests the existence of two stationary solutions of the  $4f$  wave function, the normal one and a second one with a maximum outside the  $5sp$  shell. Bringer<sup>16</sup> has disputed this model by showing that for atomic Ce the energy increases monotonically with the extent of the  $4f$  wave function. He parametrizes the  $4f$  wave functions such that the second moment  $\langle r^2 \rangle$  is fixed and then minimizes the Hartree-Fock energy by determining the remaining parameters. In the following we extend these calculations to Ce impurities in Pd. Analogously to Bringer we constrain the second moment of the  $f$  density on the impurity site:

$$\lambda \left\{ \int_{\text{WS}} r^2 n_f(\vec{r}) d^3r - \langle r^2 \rangle \int_{\text{WS}} n_f(\vec{r}) d^3r \right\}. \quad (7)$$

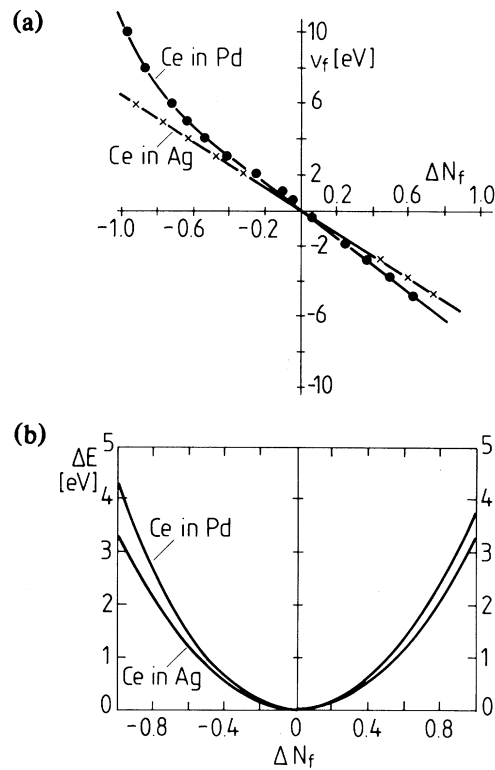


FIG. 1. (a) The Lagrange parameter  $\nu_f$ , which controls the  $f$  occupation  $N_f$ , as a function of  $\Delta N_f$  for Ce impurities in Pd and Ag (semirelativistic calculation). (b) The energy difference  $\Delta E(N_f)$  vs  $\Delta N_f$  for Ce in Pd and Ag.

This leads to a parabolic potential  $\lambda(r^2 - \langle r^2 \rangle)$  in the Kohn-Sham equations which, for  $\lambda < 0$ , repels the  $f$  electrons in the inner region  $r^2 < \langle r^2 \rangle$  and attracts them to the outer region  $r^2 > \langle r^2 \rangle$ . The energy difference  $\Delta E(\langle r^2 \rangle)$  is again calculated from the Hellmann-Feynman theorem and is plotted in Fig. 2 versus  $\langle r^2 \rangle$ . No second minimum is found. Note that contrary to the atomic calculation the  $f$  occupation  $N_f$  is not fixed, but allowed to relax in order to minimize the energy. As shown in Fig. 2 (right-hand scale)  $N_f$  strongly decreases with increasing  $\langle r^2 \rangle$ . This indicates that it is energetically more favorable to promote the  $f$  electrons into the conduction band than to shift them to the region outside the  $5sp$  shell. More details about the present calculations will be published elsewhere.

In conclusion, we have presented an extension of density-functional theory to the lowest states compatible with some arbitrary constraints. We have demonstrated that such constrained ground-state calculations can give interesting information about excitation properties, especially about charge and

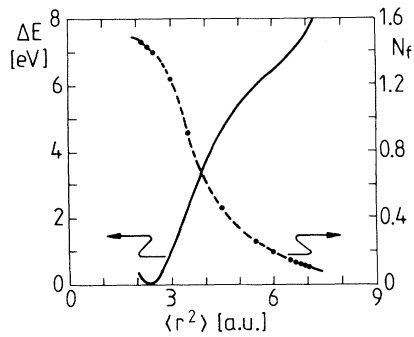


FIG. 2. The energy change  $\Delta E$  (left-hand scale) and the  $f$  occupation  $N_f$  (right-hand scale) vs the second moment of the  $f$ -charge density for a Ce impurity in Pd (nonrelativistic calculation).

magnetization fluctuations in solids.

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<sup>(a)</sup>On leave from Nara Medical University, Nara, Japan.

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