Long-range contributions to the total energy of an impurity in an extended substrate

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A study of the total energy of an isolated impurity in an extended substrate is presented. The approach is based on the Green's function embedding method within the density functional theory framework. We explicitly take care of the influence of an infinite substrate and introduce the contributions to the total energy of an isolated impurity deriving from long range charge density oscillations. Total energies for a substitutional Al atom in Mg and Na bulks calculated in this way are compared with those obtained by expressions limited to smaller regions, focusing on accuracy and convergence as function of the self-consistent calculation volume. A faster and variational (monotonic) convergence is obtained by using the energy expression proposed in this paper.

I. INTRODUCTION

The physics of atomic impurities in an extended substrate comprise a variety of very interesting phenomena. In the case of a magnetic impurity in a normal metal several theoretical and experimental efforts have been devoted to the Kondo problem. In surface physics adatom bonding is crucial to the understanding of crystal growth, of the magnetism of thin film, and of chemisorption induced reconstruction.

In all these fields the knowledge of the total energy is necessary to supply the energetics, the most stable configuration of the system and the input to determine other physical properties for comparison with experiments (for example, the superconducting transition temperature or the crystal growth rate). Presently the total energy can be calculated within a first principle framework based on density functional theory (DFT).[1] Most of such calculations for defects and impurities employ the supercell geometry.[2] In this approach a 3D array of cells (or repeated slabs) or a 2D one (for adatoms) describes the physical system as a periodic one. Within the LDA-GGA approach the supercell method performs efficiently. For example, results of the formation energy of vacancies and impurities in a realistic metal, obtained by the supercell geometry, are in very good agreement with the experimental ones. The reported computational error is of the order of 30 meV for a 32 atom supercell.[3] But impurities may be extremely diluted[4] and a very low coverage of adatoms may result into appreciable induced surface resistivities,[5] while one single adatom may cause measurable surface long range charge density oscillations.[6,7] Such effects ask for the treatment of a single isolated defect in an extended substrate. Calculations based on the supercell geometry achieve a level of description equivalent to that of a truly single impurity only when the volume of the system is very large. In practice, the size of this volume is determined by the strength of the perturbation induced by the impurity. If such a disturbance is not fully screened the calculated energy may depend on the slab thickness.[8] To correctly account for these long range effects a too large volume and hence a too high computational cost may be required. So it is interesting to study geometries other than the supercell to describe the physical properties of single isolated perturbations. A possible choice is a cluster representation of the substrate. But in such finite size models the convergence of physical properties with the cluster size and geometry is not smooth,[9] and a very large volume of the system is needed too.[10]

Methods based on the use of Green's functions are most suitable for treating the problem of a single perturbation in an extended substrate. All these methods share the same approach, i.e., they solve the problem in a finite volume taking into account the infinite host via appropriate boundary conditions for the Green's function. The Dyson equation,[11,12] the Korringa-Kohn-Rostoker method,[13,14] and the embedding method[15,16] are well known examples. Once the single particle Green's function of the interacting system is available one could compute the total energy. But computational difficulties are usually more severe in this case than for the supercell one. Consequently very few *ab initio* calculations of total energies have been worked out by the Green's function approach.

In this paper we shall compute the total energy of an isolated impurity in an infinite solid by the embedding Green function method.[15] We shall focus on the total energy convergence with the calculation parameters, especially as a function of the embedding region volume. By exploiting the properties of the Green function, we shall introduce a total energy expression which takes also into account the long-range contributions of the extended substrate beyond the region in which the DFT problem is solved. Our infinite solid is modeled by jellium. Though we do not expect jellium to allow for calculating realistic impurity formation energies, this model is very convenient to study in a systematic way to which extent the long-range perturbation induced by the defect affects the total energy of the system. This because one can vary the size of the region where the DFT calculation is performed in a continuous manner. By comparing total energies computed by the new expression with those obtained with the grand-canonical functional,[17] and with that of Puska *et al.*,[18] we show that the proposed expression allows one to obtain a faster converging variational (monotonic) total energy within a computational accuracy, which may range between 1–20 meV according to the substrate.

Section II is devoted to illustrating how long-range charge density oscillations may be taken into account by the Green's function embedding method of Inglesfield[15,19] within the DFT framework. Section III deals with a description of the different expressions describing the impurity total energies, and Sec. IV presents results for an Al substitutional impurity in Mg and Na bulk jellium. Finally Sec. V outlines the conclusions of this paper.

II. SCHEME OF THE CALCULATION

We adopt an approach based on the embedding method[15] (EM) in the framework of density functional theory (DFT). This method is particularly suitable for the description of a nonperiodic isolated perturbation inside a bulk material or at the surface of a solid, because it explicitly takes into account the effects of an infinite/semi-infinite substrate. In this approach the whole space is divided into two regions: an embedding region containing the perturbation, e.g., due to an impurity, (region I) and the remaining space (region II). The solution of the electronic problem in region II is assumed to be known and the method derives a self-consistent single particle equation for the electronic system in region I, for example in the Kohn-Sham (KS) formulation of DFT. The effects of an infinitely extended substrate outside region I enters this (embedding) equation via a nonlocal energy dependent potential, the embedding potential v_{emb}, defined on the surface S of region I. This potential guarantees the correct matching of the electron wave functions at the boundaries of the two regions. One can recast the problem in terms of a one particle Green's function. Hence the embedding equation becomes an equation for G_I, the restriction of the global Green's function in I+II, G_{I+II}, to region I, while v_{emb} is defined as the inverse of the Green's function G_{II} on S for a particular choice of its boundary conditions. For a thorough description of the embedding method we refer to Inglesfield.[15,20]

It is well known that any localized perturbation leads to a nonlocal perturbation of the electronic system (for example, charge density oscillations, wave function phase shifts, etc.).[21] Consequently the study of this system would require the solution of the KS equation in a very large, in principle infinite, volume. To tackle this difficulty one can apply the EM assuming that most of the perturbation be screened inside a large enough volume V_I, i.e., that of region I. So we are led to introduce an approximated description of the effects that the substrate in region II plays on region I. The simplest one (zero order) is to assume G_{II} to be the Green's function of the unperturbed system G_{II}^0, that is to substitute the exact embedding potential with that obtained from G_{II}^0. In other words the effective potential of the KS equation in the region II is the unperturbed one. In this way we determine v_{emb} and then calculate the self-consistent solution for G_I. This solution is not in agreement with the previous hypothesis which considers region II to be unperturbed. Indeed the Fermi energy is pinned by the infinite substrate and a flow of charge between the two regions takes place. Such charge transfer is neglected in assuming region II unperturbed. Consequently there is an overall charge non-

neutrality of the system. To take into account the effect of the incomplete screening of the perturbation, we should introduce in region II a correction ΔG_{II}^0 to G_{II}^0. Then we should iterate the calculation of G_I with a new embedding potential $v_{emb} + \Delta v_{emb}$ obtained from $G_{II}^0 + \Delta G_{II}^0$ and so on. The implementation of this iterative procedure is by no means straightforward[22] and at a certain point even useless. By choosing a large enough embedding volume V_I, we can always reduce the importance of Δv_{emb} in the calculation of G_I. In fact the resulting correction to G_I would be a higher order one which we can safely neglect. On the contrary the perturbation induced in region II can be significant and need be considered carefully. The wavelength of the Friedel charge density oscillations, obeying asymptotically an inverse third power law in bulk,[6,23] $\lambda = \pi/k_F$ (k_F being the Fermi wave vector), may be very long (in the case of Na described by the jellium model $\lambda \simeq 6.4\, a_0$, a_0 being the Bohr radius). This means that the lack of charge neutrality could be appreciable, even if we had chosen a very large embedding volume for region I.

In this work we avoid the formidable task of solving self-consistently the KS equation in region II and consider the zero order approximation for the embedding potential v_{emb}. We improve on the description of the substrate outside the embedding region by taking into account a first order correction ΔG_{II}^0 to G_{II}^0, which is obtained as the continuation of G_I via a matching Green's function technique. The Appendix is devoted to the analysis of this extrapolation procedure. Once a quantitatively satisfactory expression for the Green's function G_{I+II} in I and II is obtained, the charge density $\rho(\mathbf{r})$ becomes available all over the space. Then the total energy calculation can be performed in the frame of any DFT approximation for the exchange-correlation functional.

We point out that so far the only simplifying hypothesis we make is to neglect the perturbation of the effective potential in II and the subsequent modification of the embedding potential acting at the surface S of region I. The importance of such perturbation is progressively reduced as the volume of region I is increased. As a consequence, in this scheme of calculation, the embedding volume V_I is the crucial physical parameter that drives the convergence of the calculated solution. Of course, the finite dimension of the basis set on which we project the Hamiltonian is another aspect which may influence the final solution. But, as discussed at the beginning of Sec. IV, such an effect becomes negligible with a suitable choice of the dimension of the basis set. Therefore we shall focus on accuracy and convergence as function of V_I.

III. THE IMMERSION ENERGY OF AN IMPURITY

We are interested in a first principle calculation of the total energy of an isolated impurity in an infinite solid, i.e., of a bulk vacancy, of a bulk interstitial or substitutional impurity, and of an adsorbate at a solid surface. We recall that within the supercell framework, the formation energy ΔE_{form}^i of an additional atom (interstitial impurity), is defined as

$$\Delta E_{form}^i = E(N, A, V) - E(N, V_0) - E(A), \quad (1)$$

where $E(N,A,V_0)$ and $E(N,V)$ are the total energies of the supercells of volume V_0 containing N host atoms, and V with N atoms plus the impurity A, respectively; $E(A)$ is the energy of the free atomic defect. For a substitutional impurity Eq. (1) has to be modified in following way:

$$\Delta E_{\text{form}}^s = E(N-1,A,V) - E(N,V_0) + E(B) - E(A), \quad (2)$$

where $E(B)$ is the energy of the free substituted impurity. For a vacancy Eqs. (1) or (2) are readily implemented. Note that each term in Eqs. (1) and (2) is finite because the supercell has a finite volume, and hence the concentration of impurities is finite too. As the formation energy is customarily defined at zero pressure, the relaxed volume V should enter the expression for $E(N,A,V)$. If we want to treat an isolated perturbation by this method, we observe that Eqs. (1) and (2) give the proper result in the thermodynamic limit N, $V \simeq V_0 \to \infty$, though a DFT calculation does not appear feasible.

In our approach we indeed deal with a single defect in an infinitely extended system without introducing any artificial periodicity. Hence the formation energies of an interstitial and of a substitutional impurity are those defined in Eqs. (1) and (2), where N, V, and V_0 are infinite. Obviously the first two terms on the right hand of Eqs. (1) and (2) are diverging quantities. To make such calculations viable it is necessary to introduce a reference system R and compute the energy differences $\Delta E_{\text{imp}} = E_{\text{imp+sub}} - E_R$ and $\Delta E_{\text{unp}} = E_{\text{unp}} - E_R$, with respect to that of R. $E_{\text{imp+sub}}$ and E_{unp} represent the total energy of the system constituted by the impurity interacting with an extended host and by the unperturbed extended host, respectively. Of course a possible choice may be $E_R = E_{\text{unp}}$. We wish to stress that the energy E_{unp} represents the calculated one, for example by a DFT self-consistent approach, for the system without the impurity. So its result depends on the accuracy and the convergence parameters of the calculation. On the other hand the reference system can be chosen arbitrarily once its asymptotic behavior reflect that of the unperturbed substrate. With such a choice ΔE_{imp} and ΔE_{unp} are finite. To this aim it will be more convenient to select a reference system in which the energy can be calculated in the simplest way and represents only an additive constant in the formation energy. In this way one can study the variation of ΔE_{imp} and ΔE_{unp} with the computation parameters without any spurious contributions from the reference system. We also point out that in this description the impurity concentration is zero and substrate macroscopic relaxation effects may be safely ignored.

In the following we shall present a total energy expression, which does not only take into account the lack of charge neutrality, but also the contribution of the extended substrate outside the embedding region. We consider in detail the energy difference $\Delta E_{\text{imp}} = E_{\text{imp+sub}} - E_R$ for a bulk defect, referred to the infinite reference system R. It can be written as the sum of the kinetic, the Coulomb and the exchange-correlation contributions

$$\Delta E_{\text{imp}} = E_{\text{imp+sub}} - E_R = \Delta E_{\text{kin}} + \Delta E_{\text{Coul}} + \Delta E_{\text{xc}}, \quad (3)$$

where we define

$$\Delta E_{\text{kin}} = \int_{-\infty}^{\epsilon_F} [\sigma(\epsilon) - \sigma^0(\epsilon)] \epsilon \; d\epsilon$$
$$- \int_{\mathbb{R}^3} (\rho_- v_{\text{eff}} - \rho_-^0 v_{\text{eff}}^0) d^3 r, \quad (4)$$

$$\Delta E_{\text{Coul}} = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'$$
$$- \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho^0(\mathbf{r})\rho^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r', \quad (5)$$

$$\Delta E_{\text{xc}} = \int_{\mathbb{R}^3} (\rho_- \epsilon_{\text{xc}} - \rho_-^0 \epsilon_{\text{xc}}^0) d^3 r. \quad (6)$$

$\sigma(\epsilon)$ is the density of states (DOS) and $\rho = \rho_- + \rho_+$ the charge density with an electronic ρ_- and a nuclear contribution ρ_+. The effective potential of the KS equation for the impurity-substrate system is v_{eff}, in which the exchange-correlation term is calculated in the local density approximation (LDA) of Ceperley and Alder.[24] Consequently Eq. (6) describes ΔE_{xc} with the well known LDA expression. The 0 apices denote the same quantities for the reference system. As regards the kinetic contribution, the first term on the right-hand side of Eq. (4) requires the global induced density of states (IDOS), $\sigma(\epsilon) - \sigma^0(\epsilon)$, of the system which can be evaluated by means of Lloyd's formula[25]

$$\Delta\sigma(\epsilon) = \sigma(\epsilon) - \sigma^0(\epsilon) = - \frac{1}{\pi} \text{Im} \frac{d}{d\epsilon} \ln \det \frac{G(\epsilon)}{G^0(\epsilon)}, \quad (7)$$

where $G(\epsilon)$ and $G_0(\epsilon)$ are the Green's functions of the interacting and of the reference system, respectively. Each of the three contributions in Eq. (3) involves single or double integrations which calls for ρ over the whole $\mathbb{R}^3$ space. Since the self-consistent computation is performed in a finite (embedding) volume, the calculated expression of ρ_- is an approximate one, which differs from the exact one, say by $\delta\rho$. As already pointed out, no charge conservation is imposed, and we define the following excess/defect of the global charge in the whole (impurity plus the extended substrate) system as

$$\Delta Q_{\text{glob}} \equiv \int_{\mathbb{R}^3} \delta\rho(\mathbf{r}) d^3 r = \int_{-\infty}^{\epsilon_F} \Delta\sigma(\epsilon) d\epsilon - Z \neq 0, \quad (8)$$

where Z represents the variation of positive charge in the system determined by the impurity. The equality between the two integrals follows from the charge neutrality of the reference system and of the perturbed one if solved exactly. The magnitude of ΔQ_{glob} may signal the quality of the approximations in the calculated solution. Of course also the charge in the embedding volume is not conserved and we label such an excess/deficit by ΔQ_{loc}. In the following we denote with $v_{\text{Coul}}(\mathbf{r})$ the electrostatic potential of the system

$$v_{\text{Coul}}(\mathbf{r}) \equiv \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' = v_{\text{eff}}(\mathbf{r}) - v_{\text{xc}}(\mathbf{r}). \quad (9)$$

The energy functional of Eq. (3) is not variational with respect to the electronic charge density, because the KS equations are derived in a DFT framework assuming charge conservation.[26] If charge is not conserved as in the EM, such functional also becomes dependent on the choice of the energy reference. As shown by Drittler *et al.*,[17] a generalized energy functional which includes a grand-canonical correction to Eq. (3) must instead be used:

$$\Delta E_{\mathrm{imp}} = \Delta E_{\mathrm{kin}} + \Delta E_{\mathrm{Coul}} + \Delta E_{\mathrm{xc}} + \epsilon_F \Delta Q_{\mathrm{glob}}. \qquad (10)$$

This correction may restore global neutrality by placing uniformly the charge ΔQ_{glob} at the Fermi level. In principle, once this correction is considered, the functional is again variational and independent of the choice of the energy reference. However, this implies the knowledge of the electronic charge density ρ_- in the whole infinite volume, and the assumption that the exact Fermi level of the system may be obtained by $\delta E / \delta \rho_-$ even if the above quantities are calculated self-consistently only in a finite volume. Therefore it is clear that the approximations introduced in a DFT calculation of the interaction energy between an impurity and an extended substrate may affect the variational character of well established expressions. To get insight into this problem we shall discuss and compare results determined by three energy expressions, which can be of working use. We refer to them as the semilocal one, that of Puska *et al.*,[18] and a new one suggested in this paper. We shall see that none of them is fully variational, but that the third one achieves an excellent level of variationality, once a computational error in the total energy is assigned. In the first functional, the electronic charge density ρ_- is assumed to be unperturbed outside the volume of the self-consistent calculation V_{I}, so that the space integral of kinetic, Coulomb, and exchange-correlation terms in Eq. (10) need not be performed over $\mathbb{R}^3$ but only inside V_{I}. The energy expression in Eqs. (4)–(6) takes the form

$$\Delta E_{\mathrm{imp}} = \int_{\epsilon_v}^{\epsilon_F} [\sigma(\epsilon) - \sigma^0(\epsilon)] \epsilon d\epsilon - \int_{V_{\mathrm{I}}} (\rho_- v_{\mathrm{eff}} - \rho_-^0 v_{\mathrm{eff}}^0) d^3 r$$
$$+ \frac{1}{2} \int_{V_{\mathrm{I}}} (\rho \ v_{\mathrm{Coul}} - \rho^0 \ v_{\mathrm{Coul}}^0) d^3 r$$
$$+ \int_{V_{\mathrm{I}}} (\rho_- \epsilon_{\mathrm{xc}} - \rho_-^0 \epsilon_{\mathrm{xc}}^0) d^3 r + \epsilon_F \Delta Q_{\mathrm{glob}}. \qquad (11)$$

An improved approximation is that of Puska *et al.*[18] In this scheme ρ_- is still assumed to be unperturbed outside V_{I} but a first order correction is introduced in the calculation of ΔE_{xc}:

$$\int_{\mathbb{R}^3 - V_{\mathrm{I}}} (\rho_- \epsilon_{\mathrm{xc}} - \rho_-^0 \epsilon_{\mathrm{xc}}^0) d^3 r$$
$$= \int_{\mathbb{R}^3 - V_{\mathrm{I}}} [\Delta \rho_- \epsilon_{\mathrm{xc}} + \rho_-^0 (\epsilon_{\mathrm{xc}} - \epsilon_{\mathrm{xc}}^0)] d^3 r$$
$$\simeq \int_{\mathbb{R}^3 - V_{\mathrm{I}}} (\Delta \rho_- \epsilon_{\mathrm{xc}}^0 + \rho_-^0 \epsilon_{\mathrm{xc}}'^0 \Delta \rho_-) d^3 r$$
$$\simeq -\bar{v}_{\mathrm{xc}}^0 \Delta Q_{\mathrm{loc}}(V_{\mathrm{I}}), \qquad (12)$$

where $\Delta \rho_- = \rho_- - \rho_-^0$, $\Delta Q_{\mathrm{loc}}(V_{\mathrm{I}}) = \int_{V_{\mathrm{I}}} \Delta \rho_- d^3 r - Z$, and $\bar{v}_{\mathrm{xc}}^0$ is the mean value of the exchange-correlation potential. Equation (12) follows from the assumption of global charge neutrality. Charge non-neutrality due to the finiteness of the embedding region is already included in the grand-canonical correction. Consequently the second energy expression is

$$\Delta E_{\mathrm{imp}} = \int_{\epsilon_v}^{\epsilon_F} [\sigma(\epsilon) - \sigma^0(\epsilon)] \epsilon d\epsilon - \int_{V_{\mathrm{I}}} (\rho_- v_{\mathrm{eff}} - \rho_-^0 v_{\mathrm{eff}}^0) d^3 r$$
$$+ \frac{1}{2} \int_{V_{\mathrm{I}}} (\rho \ v_{\mathrm{Coul}} - \rho^0 \ v_{\mathrm{Coul}}^0) d^3 r + \int_{V_{\mathrm{I}}} (\rho_- \epsilon_{\mathrm{xc}}$$
$$- \rho_-^0 \epsilon_{\mathrm{xc}}^0) d^3 r - \bar{v}_{\mathrm{xc}}^0 \Delta Q_{\mathrm{loc}}(V_{\mathrm{I}}) + \epsilon_F \Delta Q_{\mathrm{glob}}. \qquad (13)$$

Except for the band integral in the kinetic term and the grand-canonical correction, both expressions (11) and (13), are essentially finite volume energy calculations. On the other hand, while the self-consistent calculation must necessarily be performed in finite volume V_{I}, that of the energy can in principle be extended to an infinite volume. We wish to propose a new expression, whose scope is to supply a better total energy for an impurity in an extended host. It will take into account the contributions of integrals in the volume $\mathbb{R}^3 - V_{\mathrm{I}}$ by considering an improved ρ_- with respect to the unperturbed one outside V_{I}. We extrapolate ρ_- all over the space according to the procedure described in the Appendix by means of the matching Green's function technique. We start from the embedding self-consistent solution for ρ_- inside V_{I}, and we generate its continuation by using the unperturbed potential v_{eff}^0 outside the embedding region as in Eqs. (A19) and (A20). We expect our results for the total energy to show a variational behavior at a much better level of accuracy, i.e., monotonic and decreasing by increasing volume V_{I} of the self-consistent treatment, than those of Eqs. (11) and (13). In practice, we perform calculations by fixing a level of accuracy of the total energy *a priori*. Then we truncate the integration in Eqs. (4)–(6) at a volume $V_{\mathrm{I}} + V_{\mathrm{II}}$, the volume V_{II} being outside the embedding region and bounded by it. The size of V_{II} depends on the required level of accuracy and the screening properties of the substrate. The new energy expression is

$$\Delta E_{\mathrm{imp}} = \int_{\epsilon_v}^{\epsilon_F} [\sigma(\epsilon) - \sigma^0(\epsilon)] \epsilon \, d\epsilon$$

$$- \int_{V_I + V_{II}} (\rho_- v_{\mathrm{eff}} - \rho_-^0 v_{\mathrm{eff}}^0) d^3 r + \frac{1}{2} \int_{V_I + V_{II}}$$

$$\times \int_{V_I + V_{II}} \frac{\rho(\mathbf{r})\rho(\mathbf{r}') - \rho^0(\mathbf{r})\rho^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r'$$

$$+ \int_{V_I + V_{II}} (\rho_- \epsilon_{\mathrm{xc}} - \rho_-^0 \epsilon_{\mathrm{xc}}^0) d^3 r$$

$$- \bar{v}_{\mathrm{xc}}^0 \Delta Q_{\mathrm{loc}}(V_I + V_{II}) + \epsilon_F \Delta Q_{\mathrm{glob}}. \tag{14}$$

Since, as explained in Sec. II, we approximate $v_{\mathrm{eff}} = v_{\mathrm{eff}}^0$ outside the embedding region in volume V_{II}, it follows that $\int_{V_{II}} (\rho_- v_{\mathrm{eff}} - \rho_-^0 v_{\mathrm{eff}}^0) d^3 r = \int_{V_{II}} (\rho_- - \rho_-^0) v_{\mathrm{eff}}^0 d^3 r.$

In the case of a jellium bulk impurity calculation, the convenient reference system is the ideal jellium for which the total charge density $\rho^0 = 0$ everywhere and $v_{\mathrm{eff}}^0 = v_{\mathrm{xc}}^0$ is a constant. Furthermore the kinetic term is independent of the choice of the energy reference and setting $v_{\mathrm{eff}}^0 = 0$ the second integral over V_{II} can be avoided. Exploiting the spherical symmetry in the Coulomb term, Eq. (14) can be simplified in this way:

$$\Delta E_{\mathrm{imp}} = \int_{\epsilon_v}^{\epsilon_F} [\sigma(\epsilon) - \sigma^0(\epsilon)] \epsilon \, d\epsilon - \int_{V_I} (\rho_- v_{\mathrm{eff}} - \rho_-^0 v_{\mathrm{eff}}^0) d^3 r$$

$$+ \frac{1}{2} \int_{V_I} \int_{V_I} \frac{\rho(r)\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r'$$

$$+ \int_{V_{II}} \frac{\Delta \rho_-(r) \Delta Q_{\mathrm{loc}}[V(r)]}{|r|} d^3 r$$

$$+ \frac{1}{2} \int_{V_{II}} \int_{V_{II}} \frac{\Delta \rho_-(r) \Delta \rho_-(r')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r'$$

$$+ \int_{V_I + V_{II}} (\rho_- \epsilon_{\mathrm{xc}} - \rho_-^0 \epsilon_{\mathrm{xc}}^0) d^3 r - v_{\mathrm{xc}}^0 \Delta Q_{\mathrm{loc}}(V_I + V_{II})$$

$$+ \epsilon_F \Delta Q_{\mathrm{glob}}. \tag{15}$$

IV. RESULTS

We apply the energy expressions discussed in the previous section to a single impurity in a bulk metal, where the extended substrate is described by jellium. Of course this choice does not allow for a realistic calculation of the impurity formation energies. However, the general character of this substrate provides a benchmark system in which the long-range effects on the total energy can be analyzed in a systematic and computationally agile way.

In particular, we investigate the convergence of the total energy calculation of a substitutional impurity, by using the various approximations discussed in the previous section. First we deal with an Al substitutional defect in a Mg substrate. Our choice for such a system is motivated by the
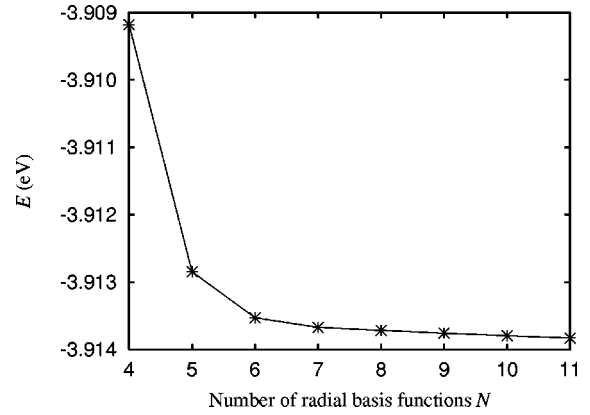

FIG. 1. Energy variation of a substitutional Al defect in Mg jellium bulk with respect to the number $\bar{N}$ of radial functions of the basis set.

attempt to consider a most general case. In fact Al is an atom which may form bonds of no specific ionic character, and Mg is a jellium metal of intermediate density $\rho^0 = 1.268 \times 10^{-2} \, a_0^{-3}$. We create a vacancy in jellium by taking away a sphere of positive background of radius $r_s = 3.35 \, a_0$, containing exactly the valence electrons of the Mg substituted atom. The energy of the reference system is that competing to an infinite uniform jellium with a vacancy, plus that of the isolated Al atom (-6566.373 eV).[27] So, we can consider ΔE_{imp} as the variation in the total energy when an Al atom occupies a vacancy inside a jellium bulk.

A linearized augmented plane wave (LAPW) basis set describes the solution of the KS equation.[16] All calculations are performed choosing an angular expansion in spherical harmonics up to $l = 9$. The results are unaffected for a larger l expansion. Outside the muffin tin of radius $r_{\mathrm{MT}} = 2.8 \, a_0$, the radial part of the LAPWs is expanded on a set of spherical Bessel functions $j_0(k_n r)$, where $k_n = n\pi/\bar{d}$ for $n = 1, N$ ($N = 14$) and $\bar{d}$ is suitably chosen larger than the radius s of the embedding region. $k_N^2/2$ is the kinetic energy cut off. In all our energy calculation by Eq. (14) it is enough to fix the radius of the volume V_{II} at 100 a_0 (for details see the Appendix). In Fig. 1 we show the variational convergence of the energy calculated by Eq. (14) on increasing the dimension N of the radial set for $s = 6 \, a_0$. We observe that the LAPW method allows us to use a conveniently small number of basis functions, since convergence is achieved quickly. We have checked that for fixed s a monotonic decrease of the total energy by increasing N is obtained for any of the three energy expressions in Eqs. (11), (13), and (14). Different behaviors of the total energy calculated by those equations as function of s occur, once all the other abovementioned parameters have been chosen. This case permits a more interesting comparison of the three expressions presented in the previous section, and confirms that the embedding volume V_I is the crucial parameter to monitor the quality of the convergence of the solution, as already pointed out in Sec. II. By analyzing total energies calculated by Eqs. (11), (13), and (14), we show that the energy terms in Eq. (14), taking into account the long-range induced charge perturbation, contrib-
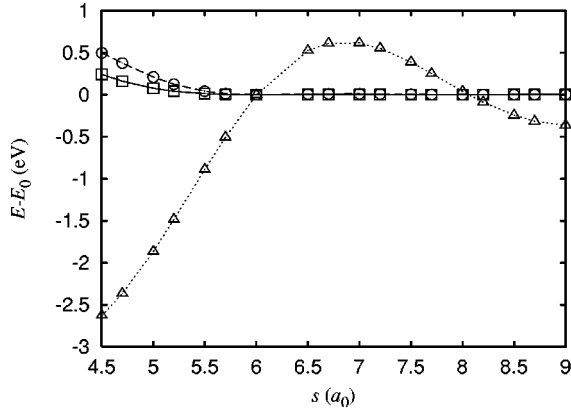
FIG. 2. Energy variation with respect to $E_0 = -3.914$ eV of a substitutional Al defect in Mg jellium bulk as function of the radius s of the embedding region. The solid line (squares) is obtained with Eq. (14), the dashed one (circles) with Eq. (13), and the dotted one (triangles) with Eq. (11).

ute to the variational behavior of the energy with respect to V_I in an essential way. In Fig. 2 we report the dependence of the total energy on the embedding radius s for the three just mentioned different energy expressions. The converged value $E_0 = -3.914$ eV is defined within the accuracy which can be obtained by our best energy expression, that in Eq. (14), for a calculation with $s = 9$ a_0. In this case it is 1 meV. The total energy worked out by the semilocal Eq. (11) (triangles) exhibits a marked damping oscillation and it differs significantly from E_0 even for larger embedding radii. That calculated by Eq. (13), which only includes an extra contribution in exchange correlation term outside the embedding region, improves the result in a considerable way. Nonetheless, within the just mentioned accuracy, this curve does not decrease monotonically. See Fig. 3 (circles) showing that energy oscillations are still present. On the other side the energy calculated by Eq. (14) (squares) displays a (monotonic) variational behavior as function of the embedding radius s. It also shows a faster convergence with respect to s, so that its value is already convergent for $s = 5.5$ a_0.

To give a quantitative estimate of the terms which contribute to $E - E_0$ in Figs. 2 and 3, we consider for example an
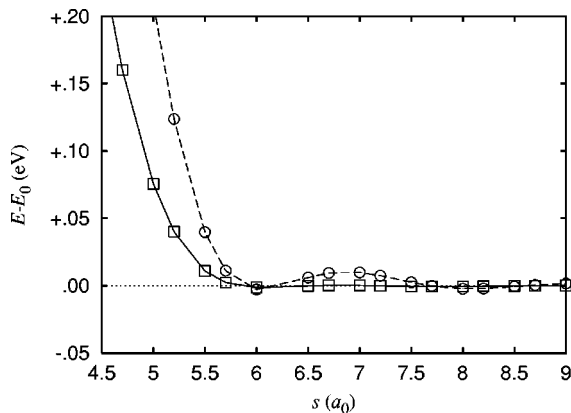

FIG. 3. Magnified energies of Fig. 2. The solid line (squares) is obtained with Eq. (14), the dashed one (circles line) with Eq. (13).
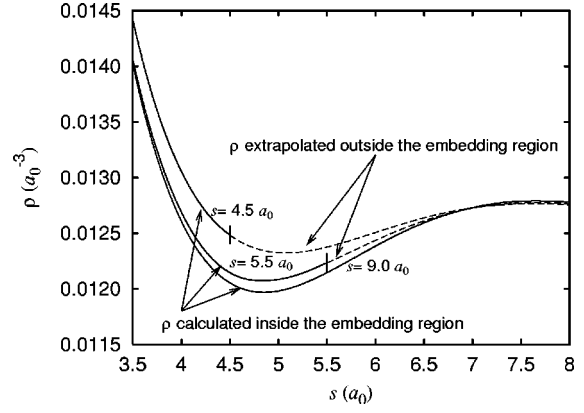

FIG. 4. Electron charge density $\rho_-(r)$ as function of r. The solid lines refer to the self-consistent result, the dashed one to the extrapolated result.

embedding region of radius $s = 9$ a_0. In Eq. (14) the contributions outside V_I are $v_{xc}^0 \Delta Q_{loc}(V_I + V_{II})$, $\int_{V_{II}} (\rho_- \epsilon_{xc} - \rho_-^0 \epsilon_{xc}^0) d^3 r$, and the Coulomb correction, whose values are 259, 109, and -3 meV, respectively. The last two contributions are calculated with the extrapolated ρ_- up to 100 a_0 via the procedure described in the Appendix. Note that the expression by Puska *et al.* in Eq. (13) only contains a contribution outside V_I of the form $v_{xc}^0 \Delta Q_{loc}(V_I) = 367$ meV. All these terms have an oscillating behavior as a function of s and the variationality of the energy in Eq. (14) stems from the inclusion of such energy corrections.

The reliability of the extrapolated ρ_- depends on the quality of the Green's function evaluated on the sphere S limiting the region I of the self-consistent embedding calculation. Of course, such Green's function could be worked out with other methods such those based on the Dyson approach;[11,12] however, as shown by Ishida and Trioni,[28] the embedding approach provides a more accurate description of the Green's function at the boundaries of the region S in which the KS equation is solved. From the comparison of the electron charge density curves obtained by calculations with different embedding radii s we can verify the convergence of the extrapolated $\rho_-(r)$ and, via this, appreciate its reliability. In Fig. 4 we display $\rho_-(r)$ calculated self-consistently inside the embedding volume (solid line) and then extrapolated outside it (dashed line) as function of the distance r from the impurity nucleus for radii $s = 4.5$ a_0, $s = 6$ a_0, and $s = 9$ a_0. In agreement with the calculated total energy we observe that all densities $\rho_-(r)$ nearly coincide for embedding radii larger than 5.5 a_0. On the other hand the curve computed with $s = 4.5$ a_0 differs in a pronounced way from the other ones. This is certainly due to a poorer screening of the impurity. On the basis of these results one can safely reduce for this system the radius of V_I from $s = 9$ a_0 to $s = 5.5$ a_0. But we point out that the optimum embedding volume V_I depends on the system under investigation. To illustrate this point, consider a less favorable situation of a substitutional impurity, e.g., an Al atom in a more dilute jellium Na-like substrate, where larger charge oscillations may persist far away from the impurity. We have worked out the total energy as function of s for the three energy expressions in
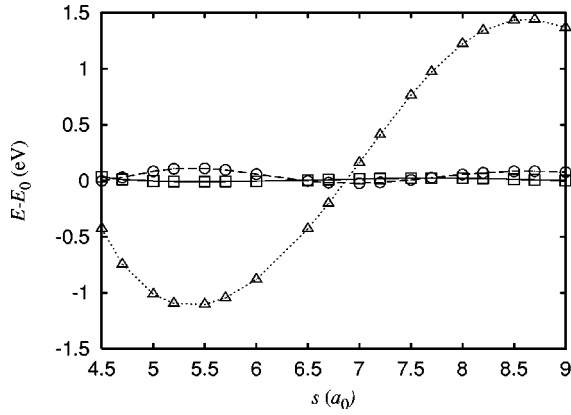
FIG. 5. Energy variation of a substitutional Al defect in Na jellium bulk as function of s. Within the accuracy described in the text the converged value is $E_0 = +6.909$ eV. Lines and symbols are the same as in Fig. 2.

Eqs. (11), (13), and (14) by a calculation with the same parameters as before. We report them in Fig. 5. Here the energy oscillations are much larger than in the previous case by using Eqs. (11) and (13), and are still appreciable within an accuracy of 20 meV for $s = 9$ a_0 in the results of Eq. (14). Note that the damping of these oscillations is slower. This indicates that the volume of the self-consistent calculation should be chosen larger. Indeed the Na valence bulk density $\rho^0 = 3.93 \times 10^{-3}$ a_0^{-3} is about three times smaller than that of Mg and then much less effective in screening the impurity perturbation.

We observe that the use of the jellium substrate does not allow for calculating realistic formation energies. In comparison with results obtained for an impurity in a periodic lattice, we overestimate them. In particular we found $\Delta E_{imp}^{Al} = -3.914$ eV, and for an Mg atom in Mg jellium $\Delta E_{imp}^{Mg} = -1.770$ eV. These results give our best estimation of the formation energy $\Delta E_{form}^s = -2.144$ eV for Al in Mg bulk. On the other hand, we are confident about the accuracy of energies calculated by our approach, since we have determined free atom energies which coincide with the most recent ones.[29]

Finally we report that we have also computed the immersion energy of an interstitial He atom in jellium bulk as a function of the host density, and that there is no appreciable difference in the results computed by Eqs. (11), (13), and (14). This signals that the perturbation induced by He is well screened inside the embedding region, and we remark that the case of a substitutional impurity is generally more interesting to discuss long-range effects in the total energy problem.

V. CONCLUSIONS

In this paper we have carried out total energies calculation of atomic impurities in jelliumlike metals within the DFT framework. We deal with an infinitely extended substrate by the embedding method. We have demonstrated that a faster convergent energy calculation (with respect to the volume V_I of the region where the KS equation is solved) is obtained by

including contributions from a larger volume than V_I. They can be worked out without a self-consistent calculation in the remaining volume V_{II}, provided that an extrapolation procedure of the Green's function is implemented. The embedding approach supplies a suitable method to extend the self-consistent Green's function to the whole space, as discussed in this paper. The total energy determined in this way is variational with respect to the embedding volume.

We observe that for large enough regions of the self-consistent calculation, the long-range perturbation of the electronic charge density does not affect total energies of a bulk impurity in a relevant way. In fact the computed effects are small. On the other hand, a total energy expression capable to take into account electronic charge perturbations of a wider range could be an interesting contribution in other areas of condensed matter, where the defect induced perturbation is ill screened by the substrate. For example for adatom or localized defect at surfaces where STM experiments have stressed the existence of Friedel's charge density oscillation which extend beyond hundreds of a_0.[7,30] Implementation of the matching Green's function total energy calculation for this lower symmetry system is by no means straightforward. But we can try to estimate roughly how long range effects compare for bulk impurities and adatoms. Recall that a convenient way to assess the lack of screening of an impurity in a electronic system is given by the global charge excess/deficit ΔQ_{glob}, as discussed in this paper. We have verified that ΔQ_{glob} of an Al impurity in Mg is safely about a factor 3 times smaller than ΔQ_{glob} for an adatom on a denser (Al-like) jellium surface[19] for calculations performed in the same volumes. Therefore much more significant changes due to the long range perturbed charge density should be expected for the total energy of a surface defect.

APPENDIX: EXTRAPOLATION VIA MATCHING GREEN'S FUNCTION TECHNIQUE

The extension of the Green's function outside the embedding region for bulk jellium has been suggested by Ishida.[31] Here we present a more general derivation which is independent of a particular system. Let S be the boundary surface between two regions I and II, which represents the partition of the space. Consider the Green's function G_0 which satisfies

$$[-\nabla^2 + v(\mathbf{r}) - E]G_0(\mathbf{r}', \mathbf{r}, E) = \delta(\mathbf{r}' - \mathbf{r}), \qquad \text{(A1)}$$

with $\mathbf{r}', \mathbf{r} \in$ II. We are interested in calculating G, the Green's function which satisfies the same differential equation as G_0 in region II but with a given boundary condition on S:

$$[-\nabla^2 + v(\mathbf{r}) - E]G(\mathbf{r}, \mathbf{r}'', E) = \delta(\mathbf{r} - \mathbf{r}''), \qquad \text{(A2)}$$

$$G(\mathbf{r}_s, \mathbf{r}''_s, E) = G_I(\mathbf{r}_s, \mathbf{r}''_s, E), \qquad \text{(A3)}$$

with $\mathbf{r},\mathbf{r}'' \in \text{II}$, $\mathbf{r}_s, \mathbf{r}_s'' \in S$ and where $G_{\text{I}}(\mathbf{r}_s, \mathbf{r}_s'', E)$ is an arbitrary boundary condition. In our calculation G_{I} will be the Green's function of the self-consistent solution in region I evaluated on S. In this Appendix we shall derive the expression of $G(\mathbf{r}', \mathbf{r}'', E)$ in terms of $G_0(\mathbf{r}', \mathbf{r}'', E)$ and $G_{\text{I}}(\mathbf{r}_s, \mathbf{r}_s'', E)$. Multiplying Eq. (A1) by $G(\mathbf{r}, \mathbf{r}'', E)$ and (A2) by $G_0(\mathbf{r}', \mathbf{r}, E)$, and subtracting each other we obtain

$$G_0(\mathbf{r}', \mathbf{r}, E) \nabla^2 G(\mathbf{r}, \mathbf{r}'', E) - \nabla^2 G_0(\mathbf{r}', \mathbf{r}, E) G(\mathbf{r}, \mathbf{r}'', E)$$

$$= \delta(\mathbf{r}' - \mathbf{r}) G(\mathbf{r}, \mathbf{r}'', E) - G_0(\mathbf{r}', \mathbf{r}, E) \delta(\mathbf{r} - \mathbf{r}''). \quad \text{(A4)}$$

Now consider the volume integral in the variable $\mathbf{r}$ of Eq. (A4) over region II. Making use of Green's theorem the volume integration in the left member of Eq. (A4) can be transformed into a surface integral over S such that

$$\int_S \left(G_0(\mathbf{r}', \mathbf{r}_s, E) \frac{\partial G(\mathbf{r}_s, \mathbf{r}'', E)}{\partial n_s} \right.$$

$$\left. - \frac{\partial G_0(\mathbf{r}', \mathbf{r}_s, E)}{\partial n_s} G(\mathbf{r}_s, \mathbf{r}'', E) \right) d^2 r_s$$

$$= G(\mathbf{r}', \mathbf{r}'', E) - G_0(\mathbf{r}', \mathbf{r}'', E), \quad \text{(A5)}$$

where $\mathbf{n}_s$ is the unit vector normal to S pointing out of region II. We shall drop the energy argument since it is the same for all the Green's functions. We shall introduce a simplified notation using a center dot for the surface integral of the product of two Green's functions and omitting the argument of the surface integration and we shall distinguish the Green's function symbol in order to specify which one of the arguments of the Green's function belongs to S: $g(\mathbf{r}'')$ will be used if the first argument of $G(\mathbf{r}_s, \mathbf{r}'')$ belongs to S, $\mathcal{G}$ if both arguments belong to S as in $G(\mathbf{r}_s', \mathbf{r}_s'')$, and finally $G(\mathbf{r})$ refers to $G(\mathbf{r}, \mathbf{r}_s')$. The normal derivatives will be indicated by primed. With these notations (A5) takes the form

$$G(\mathbf{r}', \mathbf{r}'') = G_0(\mathbf{r}', \mathbf{r}'') + G_0(\mathbf{r}') \cdot g'(\mathbf{r}'') - G_0'(\mathbf{r}') \cdot g(\mathbf{r}''). \quad \text{(A6)}$$

Now set the first argument $\mathbf{r}'$ to belong to S

$$g(\mathbf{r}'') = g_0(\mathbf{r}'') + \mathcal{G}_0 \cdot g'(\mathbf{r}'') - \mathcal{G}_0' \cdot g(\mathbf{r}''). \quad \text{(A7)}$$

Using Eq. (A7) to express $g'(\mathbf{r}'')$ we can rearrange Eq. (A6) so that

$$G(\mathbf{r}', \mathbf{r}'') = G_0(\mathbf{r}', \mathbf{r}'') + G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot [(I + \mathcal{G}_0') \cdot g(\mathbf{r}'')$$

$$- g_0(\mathbf{r}'')] - G_0'(\mathbf{r}') \cdot g(\mathbf{r}'') = G_0(\mathbf{r}', \mathbf{r}'')$$

$$- G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}'') + [G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot (I + \mathcal{G}_0')$$

$$- G_0'(\mathbf{r}')] \cdot g(\mathbf{r}''), \quad \text{(A8)}$$

where $\mathcal{G}_0^{-1} = G_0^{-1}(\mathbf{r}_s, \mathbf{r}_s')$ is the surface inverse Green's function of G_0 which satisfies

$$\int_S G_0^{-1}(\mathbf{r}_s, \mathbf{r}_s') G_0(\mathbf{r}_s', \mathbf{r}_s'') d^2 r_s' = \delta(\mathbf{r}_s - \mathbf{r}_s'').' \quad \text{(A9)}$$

Now set the second argument $\mathbf{r}''$ on S in Eq. (A8):

$$G(\mathbf{r}') = [G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot (I + \mathcal{G}_0') - G_0'(\mathbf{r}')] \cdot \mathcal{G}_{\text{I}}. \quad \text{(A10)}$$

To derive Eq. (A10) we have used Eq. (A3) noting that the first two terms on the right cancel out.

Exploiting the symmetry of the Green's function with respect to the exchange of the arguments in Eq. (A10) we obtain

$$g(\mathbf{r}'') = \mathcal{G}_{\text{I}} \cdot [(I + \mathcal{G}_0') \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}'') - g_0'(\mathbf{r}'')]. \quad \text{(A11)}$$

Finally substituting Eq. (A11) in (A8) we have

$$G(\mathbf{r}', \mathbf{r}'') = G_0(\mathbf{r}', \mathbf{r}'') - G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}'')$$

$$+ [G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot (I + \mathcal{G}_0') - G_0'(\mathbf{r}')] \cdot \mathcal{G}_{\text{I}} \cdot [(I$$

$$+ \mathcal{G}_0') \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}'') - g_0'(\mathbf{r}'')]. \quad \text{(A12)}$$

This is the desired expression for the Green's function G satisfying Eqs. (A2), (A3) in terms of a generic G_0 and $\mathcal{G}_{\text{I}}$. It can be convenient to make a particular choice for the boundary condition on G_0 which simplifies Eq. (A12). In the case of embedding method calculations, it is useful to choose a G_0 which satisfies the same boundary condition of the embedding potential

$$\frac{\partial G_0(\mathbf{r}', \mathbf{r}_s, E)}{\partial n_s} = 0. \quad \text{(A13)}$$

Equation (A12) then simplifies to

$$G(\mathbf{r}', \mathbf{r}'') = G_0(\mathbf{r}', \mathbf{r}'') - G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}'')$$

$$+ G_0(\mathbf{r}') \cdot \mathcal{G}_0^{-1} \cdot \mathcal{G}_{\text{I}} \cdot \mathcal{G}_0^{-1} \cdot g_0(\mathbf{r}''), \quad \text{(A14)}$$

and $\mathcal{G}_0^{-1}$ turns out to be just the embedding potential. With this choice of G_0 the extrapolation procedure described by Eq. (A14) is readily implemented in all calculations, which adopt the embedding method, without further numerical effort. This because the embedding potential $\mathcal{G}_0^{-1}$ and the function G_0 are already ingredients of the self-consistent calculation.

In the case of jellium bulk the potential v in Eq. (A1) is a constant and an analytic expression of $G_0(\mathbf{r}, \mathbf{r}', E)$ is available:

$$G_0(\mathbf{r}, \mathbf{r}', E) = \frac{e^{ik|\mathbf{r} - \mathbf{r}'|}}{4\pi |\mathbf{r} - \mathbf{r}'|}$$

$$= -\frac{k}{i} \sum_l \frac{2l+1}{4\pi} j_l(kr_<) h_l'(kr_>) P_l(\cos \gamma),$$

$$\quad \text{(A15)}$$

where $k = \sqrt{2E}$ with a positive imaginary part if any. In Eq. (A15) j_l is the spherical Bessel function, h_l' is the spherical Hankel function of the first kind, P_l is the Legendre polynomial of angular quantum number l, $r_< = \min(r, r')$, $r_> = \max(r, r')$ and γ the angle between $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$. Exploiting the spherical symmetry of the system, such as the impurity problem treated in this paper, $G_{\text{I}}(\mathbf{r}, \mathbf{r}', E)$ can be expressed as

$$G_1(\mathbf{r},\mathbf{r}',E) = \sum_l \frac{2l+1}{4\pi} G_1^l(r,r',E) P_l(\cos\gamma). \quad (A16)$$

Applying Eq. (A12) we obtain

$$G(\mathbf{r},\mathbf{r}',E) = -\frac{k}{i} \sum_l \frac{2l+1}{4\pi} [j_l(kr_<)h_l'(kr_>)$$
$$+ C_l(E)h_l'(kr)h_l'(kr')] P_l(\cos\gamma),$$
$$(A17)$$

where $C_l(E)$ is

$$C_l(E) = -\frac{i}{k}\frac{G_1^l(s,s,E)}{h_l'(ks)h_l'(ks)} - \frac{j_l(ks)}{h_l'(ks)}, \quad (A18)$$

and s is the radius of the embedding region I. From Eq. (A17) and the following definition:

$$\rho_-(\mathbf{r}) = \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\epsilon_F} G(\mathbf{r},\mathbf{r},E)\,dE, \quad (A19)$$

the electron charge density $\rho_-(\mathbf{r})$ becomes accessible all over the space. In practice we divide the space into three regions: the embedding region I for which $r < s$, the region where our extrapolation is more relevant $s < r < \bar{s}$ (typically we chose $\bar{s} = 20\,a_0$) and the region $\bar{s} < r < \infty$ where the Friedel asymptotic behavior of $\rho_-(\mathbf{r})$ can be safely assumed. In region I we calculate $\rho_-(\mathbf{r})$ by Eq. (A19) using the Green's function obtained from the self-consistent calculation. In the intermediate region we use the Green's function determined by Eq. (A17). In the asymptotic region we use

$$\rho_-(\mathbf{r}) = \rho_-^0 + \Delta\rho_-(\mathbf{r}) = \rho_-^0 + A\frac{\sin kr}{r^3} + B\frac{\cos kr}{r^3},$$
$$(A20)$$

where the parameters A and B are calculated from a fitting of $\rho_-(\mathbf{r})$ over the range of r in the intermediate region where the discrepancy of the charge density from its asymptotic behavior could be safely neglected. The dependence of A and B on the embedding radii s can be conveniently estimated by a phase $\phi = \arctan A/B$. For the system thoroughly investigated in this paper, i.e., Al in jelliumlike Mg, and for s in between $5.5a_0$ and $9a_0$, the uncertainty in the determination of ϕ is $0.2°$ of angle at most.

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