Utilization of locally shifted potentials in approximate electronic structure calculations

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Abstract. An approximate computational scheme is proposed for treating complex systems. The proposed method relies on the quadratic approximation to the multiple-scattering theory of Korringa, Kohn and Rostoker, which allows one to implement potential shifts in the solution of the Schrödinger equation for impurities. Choosing these shifts appropriately, one can simulate various physical processes in complex systems in an efficient computational way. The efficiency of our method is demonstrated by two example calculations. In the first, we calculate the charge transfer towards (or outwards from) a 3d or a 4d single substitutional impurity in a Cu or Ni host metal. In the second example, we calculate the binding energies of the 2s electrons of 3d atoms in solids in a quasi-adiabatic approximation.

1. Introduction

The recent development of the order-N, $\mathcal{O}(N)$, algorithms and the availability of increased computer capacities nowadays have allowed electronic structure calculations to employ unit supercells containing very large numbers of atoms [1, 2]. These advantages have offered new possibilities in the study of impurity systems and alloys, and results obtained from their utilization can be used for testing simpler computational approaches and various model approximations, which may be applicable to more complex problems [3]. Appearing to be of special interest is the case of physical processes in complex systems which exhibit a high degree of localization and therefore can be simulated by single-electron potential shifts localized in one or more regions of the system.

   One example case stems from the study of the effect of the point-charge electrostatics on the properties of alloys. For this problem, Faulkner and collaborators [1–3], using results obtained with the $\mathcal{O}(N)$ algorithms, have demonstrated the range of applicability and the limitations of simpler models [4–8] proposed within the coherent potential approximation (CPA). In particular, first-principles calculations have justified the method of Johnson and Pinski [5], which is based on the picture in which the net charge Q_i at the ith site of an alloy is almost completely screened by charge transferred to or from the atoms on the nearest-neighbour shell and hence the contributions to the Coulomb potential come primarily from the first shell. This conclusion is not correct for every individual site in the alloy, but it has

been shown to be true when the contributions to the potential are averaged over all sites occupied by the same species of atom [3]. As a result, the effect of the screening charge (related to the site charge Q_i) can be simulated by a shell of charge $-Q_i$ at the distance of the nearest-neighbour shell. This in turn modifies the potential of the atom at the ith site by a potential shift δV_i given by

$$\delta V_i = -\frac{Q_i}{R_1} \tag{1}$$

where R_1 is the distance from a first-nearest neighbour to the ith site. From a practical point of view, equation (1) can be viewed in the opposite way. In particular, one could assume that equation (1) is correct for a system which exhibits charge-transfer effects and therefore that the electronic states of such a system could be accurately calculated by incorporating the point-charge electrostatics, i.e. the induced potential shifts δV_i given by equation (1), within the Schrödinger equation in an appropriate way. It is apparent, however, that such a solution to the problem has to be obtained in a self-consistent way because the charge transfers Q_i, and the corresponding potential shifts δV_i, which have to be the expected output of the solution, are taken as input parameters of the system in the proposed consideration.

In an approach similar to that described above, using a potential shift in the single-electron Schrödinger equation for an atom in a metal, one can simulate the final state of a crystal atom which undergoes an inner-electron excitation, the latter leaving the crystal atom with an inner-electron hole. It is recalled that a crystal atom with an inner-electron hole is often approximated as the $Z + 1$ impurity in a metal characterized by atoms of atomic number Z [9, 10]. Therefore, the approximate calculational scheme that is proposed for the single-impurity system, as described above, could have been equally well applied in the studies of the electronic binding energies (BEs) of bulk atoms too. However, our method allows a different approximation as well. In particular, a potential shift δV_i is used to simulate the final-state effects of the excited atom (i.e. the one with the inner-electron hole) by imposing the condition of local charge neutrality. In our present application the charge neutrality is restricted to being over the unit cell which contains the excited atom; however, as will be shown below, by imposing self-consistency in obtaining the potential shift δV_i, most of the final-state effects can be accounted for in the estimation of the inner-electron BEs.

Another interesting application of the present method is the incorporation of correlation effects beyond the local electron density approximation (LDA) and within the single-electron Schrödinger equation. This can be achieved by simulating these correlations by a potential shift (of the type of a Hubbard-U term) obtainable according to the Hubbard model [11].

A common characteristic of all of these applications is that they can be simulated by potential shifts which are applied locally and satisfy different boundary conditions, the latter implied by the system and the physical process that are considered. In the present work, after a brief presentation of our method, we will demonstrate its applicability by means of two example applications, namely, the calculation of the charge transfer associated with a 3d/4d substitutional impurity in a 3d-metal host and the calculation of the 2s BE (given relative to the free-atom state) of 3d atoms in their bulk state.

2. The method

Without loss of generality and for reasons of clarity, we present the formalism of our method in relation to the impurity problem. This is because, as was stated earlier, in going from application to application, only the boundary conditions applied to the simulation potential

shifts change, while the formulation of the problem is not affected.

The present application of the proposed new approach, as applied in the case of single-substitutional impurity systems, is implemented as follows. An impurity potential $v_i(r)$ is created and placed in the impurity cell at the lattice site R_i while the host potentials $v(r)$ are located in all of the other cells in the crystal. A series of calculations are carried out with shifted impurity potentials $v_i^{\text{shift}}(r, \zeta)$, of the form

$$v_i^{\text{shift}}(r, \zeta) = v_i(r) + \zeta \sigma_i(r) \tag{2}$$

where $\sigma_i(r)$ is a step function that is one when r is in the ith cell and zero otherwise and ζ is a constant. A net charge within the impurity cell, $Q(\zeta)$, will be obtained for each value of ζ. When the shift calculated from equation (1) with a charge $Q_i = Q(\zeta)$ is equal to the shift ζ that was used to calculate that charge, self-consistency has been achieved. Similar methods have been proposed before, either in studies of alloys [5–7, 12], or in other applications, such as in the work of Lambrecht *et al* [13], where this type of approach has been proposed as an efficient calculational method for determining energy band offsets for semiconductors.

In principle, the application of the present proposal could be difficult, because shifting a potential by $\zeta \sigma_i(r)$ in a unit cell of a crystal is not a simple thing to do. Normally, it would be necessary to make additional approximations in order to implement it, such as replacing the polygonal impurity cell by a sphere. In the present work, such approximations are avoided by making use of the advantages offered by the quadratic approach to the Korringa–Kohn–Rostoker (KKR) method, abbreviated as the QKKR method [14, 15]. The QKKR method uses scattering matrices that are not diagonal in the angular momentum indices in order to treat scattering from non-spherical potentials. In the band theory application of the method, the equations of Korringa [16], Kohn and Rostoker [17] are rewritten in such a way that the structure constants are independent of energy, by adding an energy-dependent shift, Δ:

$$\Delta = E - E_0 \tag{3}$$

multiplied by the step function, i.e., $(E - E_0)\sigma(r)$, to the potential function for each cell in the crystal. The addition of an another shift to the impurity potential, as in equation (2), is therefore extremely simple. In more detail, within the QKKR method, the potentials $v_i(r)$ and $v(r)$ take, respectively, the forms $v_i^\Delta(r)$ and $v_j^\Delta(r)$, $j \neq i$, given by the following equations:

$$v_i^\Delta(r) = v_i(r) + \Delta \sigma_i(r) \tag{4}$$

$$v_j^\Delta(r) = v(r) + \Delta \sigma_j(r) \qquad j \neq i. \tag{5}$$

Similarly, the shifted potential $v_i^{\text{shift}}(r)$ takes the form

$$v_i^{\Delta,\text{shift}}(r; \zeta) = v_i(r) + (\Delta + \zeta)\sigma_i(r). \tag{6}$$

For the crystal potential $V^\Delta(r)$ constructed from the cell potentials $v_i^{\Delta,\text{shift}}(r; \zeta)$ and $v_j^\Delta(r)$, $j \neq i$, given by equations (6) and (5), the Green's function $G_A^\Delta(E, \zeta; r, r')$ takes the form [18, 19]

$$G_A^\Delta(E, \zeta; r, r') = \sum_{L,L'} Z_L^{\Delta A}(r, \zeta)\tau_{ALL'}^{\Delta 00}(\zeta)Z_{L'}^{\Delta A}(r', \zeta) - \sum_L Z_L^{\Delta A}(r, \zeta)J_L^{\Delta A}(r', \zeta) \tag{7}$$

where L and L' are angular momentum indices. The wave functions $Z_L^{\Delta A}(r, \zeta)$ and $J_L^{\Delta A}(r, \zeta)$ are regular and irregular solutions of the Schrödinger equation in the field of the potential $v_i^{\Delta,\text{shift}}(r; \zeta)$ for the energy E_0, and the matrix $\tau_A^{\Delta 00}(\zeta)$ is given by

$$\tau_A^{\Delta 00}(\zeta) = \left[1 + \tau^{\Delta 00}(m_A^\Delta(\zeta) - m^\Delta)\right]^{(-1)} \tau^{\Delta 00}. \tag{8}$$

The matrices $m_A^\Delta(\zeta)$ and m^Δ are the inverses of the t-matrices that describe the scattering from the shifted potentials given by equations (6) and (5) respectively; they can be obtained using methods that have been explained elsewhere [14, 15]. The matrix $\tau^{\Delta 00}$ is given by a k-integration over the Brillouin zone:

$$\tau^{\Delta 00} = \frac{\Omega}{8\pi^3} \int \left[m^\Delta - B(E_0, \boldsymbol{k})\right]^{(-1)} \, \mathrm{d}\boldsymbol{k} \tag{9}$$

where Ω is the volume of the crystal and the elements of the matrix $B(E_0, \boldsymbol{k})$ are the well known structure constants of KKR band theory [16, 17] calculated for the one energy E_0.

The net charge on the impurity site $Q(\zeta)$ is obtained by integrating over the impurity cell and energy:

$$Q(\zeta) = -\frac{1}{\pi} \operatorname{Im} \int_{B_0}^{E_F} \mathrm{d}E \int_{\text{impurity cell}} G_A^\Delta(E, \zeta; \boldsymbol{r}, \boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} - Z_i. \tag{10}$$

The Fermi energy, E_F, of the host metal is used in equation (10), Z_i is the charge on the impurity nucleus and B_0 is the bottom of the conduction band.

The calculation of the charge $Q(\zeta)$ according to equation (10) and within the calculational scheme described above can be obtained at different levels of approximation. In particular, one can obtain $Q(\zeta)$ in one of the following ways.

(i) $Q(\zeta)$ is obtained as the output of a single iteration, i.e. without allowing for any charge relaxation within the impurity and host cells.

(ii) $Q(\zeta)$ is obtained at the end of a self-consistent solution for which it is assumed that the charges are frozen in every cell except in the one that contains the impurity. In this case, the self-consistent approach allows for a redistribution (relaxation) of the charge in the impurity cell, not allowed in process (i).

(iii) $Q(\zeta)$ is obtained within the self-consistent scheme described in (ii) allowing also for charge relaxation in the host cells surrounding the impurity cell. This approximation, however, will not be discussed here as it falls outside the scope of the present work, which aims to propose an efficient approximate calculational scheme applicable to complex systems.

The values of the charges in the impurity cell obtained according to the approximations (i), (ii) and (iii) will be denoted by $Q^{(x)}(\zeta)$, where $(x) = $ (i), (ii), (iii). M_1/M_2 will be used to denote the system with a substitutional impurity M_1 in the host lattice M_2.

3. Tests and discussion

The applicability of our method is firstly tested in the case of metallic systems with a single substitutional metal impurity for which accurate theoretical results are available for comparison. In particular, reported results obtained by the well developed computational methods for the single-impurity systems [20–24] are used for a quantitative test of the present method. As a second application we will demonstrate the use of the proposed theory in calculating shifts in the BEs of the inner electrons of atoms caused by changes in their local environment.

3.1. Charge transfer

Calculational tests were carried out for the single-impurity systems Ti/Cu, V/Cu, Co/Cu, Ni/Cu, Zn/Cu, Nb/Cu and Cu/Ni. In each of the first six systems the scattering parameters for the impurity atom (Ti, V, Co, Ni, Zn, Nb) were obtained from a self-consistent calculation
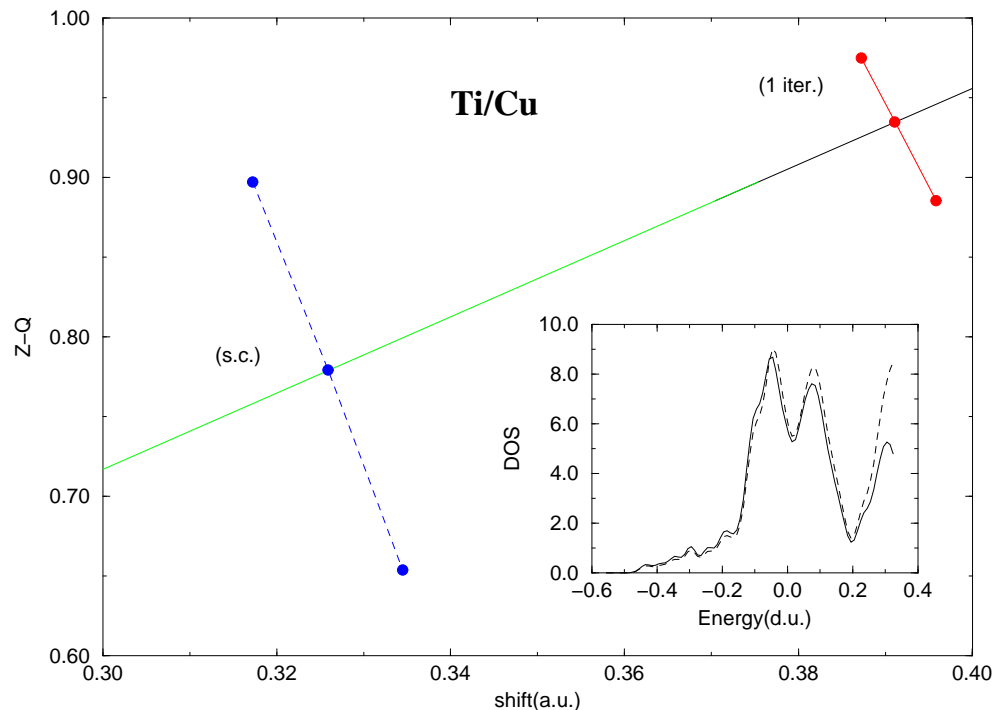
Figure 1. Results for the system Ti/Cu. The calculated charge transfer from (shown as positive) or towards (shown as negative) the impurity site obtained according to equation (10) of the text (dashed line) as a function of the potential shift applied to the impurity potential; the labels (1 iter.) and (s.c.) indicate, respectively, results obtained within the levels of approximation (i) and (ii) discussed in the text. The variation given by equation (1) is indicated by the solid line. In the inset the electron DOS as obtained according to level (i) (solid curve) and level (ii) (dashed curve) approximation are shown.

for pure Ti, pure V, pure Co, pure Ni, pure Zn or pure Nb respectively, each one of the impurities assumed to be on a fcc lattice with the pure Cu lattice constant. For the system Cu/Ni, the scattering parameters for the impurity atom (Cu) were obtained from a self-consistent calculation for pure Cu in a fcc structure with the lattice constant that of Ni. The intersection between the calculated variation of $Q^{(x)}(\zeta)$, $(x) = $ (i), (ii), versus ζ (for each impurity system) with the one describing the charge Q_i versus the shift δV_i according to equation (1) estimates the charge flow from or towards the impurity cell at the different levels of approximation. Preliminary results for the values $Q^{(i)}(\zeta)$ for selected impurities in Cu and Ni host lattices were reported in reference [25]. In the present work, we extend our method to calculations at the level of approximation (ii) described above. Our results for $Q^{(i)}(\zeta)$ and $Q^{(ii)}(\zeta)$ are presented in table 1 along with other reported data for comparison. A graphical illustration of our solution is presented in figure 1 for Ti/Cu.

It should be emphasized that charge transfer is an ill-defined quantity and much care has to be taken as regards its usage (see for example reference [28]). In particular, the charge transfer depends on the way in which the crystal space is divided (and the definition of the impurity cell). Also, the charge transfer is very sensitive to the lattice (geometric) and charge relaxation in and around the impurity cell. Furthermore, small changes in the calculated impurity charges may be caused by the different lattice constants used in the

Table 1. The calculated total charge within the impurity cell for various single-impurity systems.

Impurity system	Lattice constant (au)	Total charge within the impurity cell		
		Present work		
		One iteration, $Q^{(i)}\zeta)$	Self-consistent, $Q^{(ii)}(\zeta)$	Other work
Ti/Cu	6.76	3.07	3.221	
	6.73			$3.21^{a,b}$
				3.34^{c}
V/Cu	6.76	4.32	4.386	
	6.73			$4.33^{a,b}$
				4.49^{c}
Co/Cu	6.76	9.10	8.990	
	6.73			$8.89^{a,b}$
				8.97^{c}
Ni/Cu	6.76	10.115^{d}	10.065	
	6.73			$9.98^{a,b}$
	6.69			10.045^{c}
				10.035^{c}
Zn/Cu	6.76	11.818	11.797	
				$11.805^{e,b}$
				$11.876^{f,b}$
				$11.801^{g,b}$
	6.90			$11.795^{h,b}$
Nb/Cu	6.76	3.68	3.833	
				$3.79^{a,b}$
Cu/Ni	6.55	10.998	11.013	
				$11.02^{i,b}$
	6.69			11.007^{c}
	6.58			11.004^{c}
				$11.026^{j,b}$

[a] Reference [21].

[b] The value of the lattice constant is not reported.

[c] Reference [26]; the result obtained by the LMTO-CPA method; it refers to the charge within the atomic sphere of the impurity.

[d] This value corrects an incorrect value in a prior publication [12].

[e] The result quoted in reference [5]; it refers to a calculation that includes the first shell of neighbours.

[f] The result obtained by R Zeller and co-workers quoted in reference [5]; it refers to a calculation in which all charges remain fixed except those of the impurity atom.

[g] The result obtained by the cc-CPA method [5].

[h] References [1, 2].

[i] Reference [23].

[j] Reference [27]; it refers to the charge within the impurity Wigner–Seitz sphere while allowing for charge relaxation in the neighbouring four shells of host atoms.

various calculations. This is apparent from the reported results quoted in table 1.

While charge relaxation has been dealt with successfully by more elaborate calculational

methods [20–24], the geometric relaxation has not been resolved completely yet. The reported results for the charge transfer do not include geometric relaxation, while some of them are available with and without charge relaxation in the surrounding impurity cells. Thus, a meaningful evaluation of the results of the present method is possible by comparing them with the corresponding results included in table 1. From such a comparison, it becomes apparent that our approach gives results in very good agreement both with those obtained by the established techniques for the single-impurity problem [20–24] and with those obtained in the context of the alloy calculations [1, 2, 5–7, 26]. The agreement found between our results and those obtained by other methods is very good, especially when our results refer to those obtained within the level of approximation (ii) described above [29]. The case of Ni/Cu exhibits an interesting decline from the results obtained by means of more accurate calculations [21] while it is in excellent agreement with the results obtained within the context of the alloy calculations [26] when the latter are projected to the same lattice constant.

The difference found between the $Q^{(i)}(\zeta)$ and $Q^{(ii)}(\zeta)$ values is mainly attributable to changes of the electron DOS at the Fermi level as a result of the charge relaxation within the impurity cell. This is clearly shown in the inset of figure 1 where the electron DOS is shown at the end of the first iteration (level (i)) and at self-consistency (level (ii)). From this comparison it becomes apparent that the relaxation process (self-consistency) increases the electron DOS at the Fermi level and this is reflected as a lowering of the shift required for screening the impurity charge.

In concluding the presentation of this application, it is worth noticing that the success of our method in evaluating the charge transfer associated with a single substitutional impurity demonstrates that the idea of local screening dictated by equation (1) is, in general, as applicable in the case of single-impurity systems as it is for alloys.

3.2. Binding energy shifts of inner electrons

In a manner similar to that described above, we can use the proposed calculational scheme to calculate the BEs of the inner (core) electrons of atoms in metals. In this case, it is assumed that an excitation process excites one inner electron of a crystal atom and raises the electron to an energy equal to that of the Fermi energy of the metal. It is therefore apparent that such an excited atom takes the role taken by the impurity atom in our previous application [30].

In order to simplify the computational work in this example case, it is further assumed that during the excitation process the local charge neutrality is not disturbed. In particular, it is assumed that no charge flows out of or into the unit cell which contains the excited atom. As our calculation allows a self-consistent redistribution (relaxation) of the valence electron charge within the unit cell which contains the excited atom, it is expected that most of the final-state effects will be included in our calculation, leaving out just the effect of charge relaxation in the unit cells surrounding the excited atom. In a more accurate calculation, the restriction of the local charge neutrality, which is imposed here only within the excited unit cell, can be lifted by extending it over a region which includes the excited atom and its surrounding unit cells. These two considerations will yield different results, but, as will be shown below, final-state effects related to the charge relaxation in the cells surrounding the excited atom constitute only a small percentage of the overall bulk effect on the inner-electron BEs.

The assumed charge neutrality in the excited unit cell of the crystal is simulated by a potential shift δV_i determined self-consistently in a similar way to the one used for

calculating the charge transfer in the impurity problem. Here, however, the boundary condition dictated by equation (1) is replaced by a new one, namely by the requirement that the potential shift δV_i be such as to preserve $N_{val} + 1$ valence electrons in the excited unit cell, where N_{val} is the number of valence electrons in the non-excited crystal atom (assuming one atom per unit cell). After obtaining self-consistency in δV_i (and in the sense of the level of approximation (ii) described above), the total energy of the system containing one excited atom is calculated using Janak's [31] formalism appropriately generalized for the present case [32]. Then, subtracting the total energy of the non-excited system we obtain the BE of the excited electron with respect to the Fermi energy of the metal [33, 9].

As is well known, LDA fails to predict the correct electronic configuration of the ground state of most of the free transition metal atoms [34]. Due to this drawback and the limitations which are inherent to the LDA as regards calculating the excitation energies, the calculated electronic BEs, as obtained within the LDA, have little practical importance. However, due to expected error cancellations, LDA can, in many cases, be used to calculate changes in the electronic BEs of an atom with reasonable accuracy. These changes (called binding energy shifts (BESs)) are caused by changes in the local environment of the atom. A characteristic example, which is of much importance in surface physics, is the successful LDA-based calculation of the electronic BESs that bulk atoms undergo as they move from the bulk to the surface of a metal [35, 10].

Table 2. Calculated electronic BESs associated with the 2s electrons of bulk Ti, V, Co, Ni and Cu atoms as found relative to their BEs for the free-atom state. Our results are based on free-atom excitations employing the experimentally observed ground states which are assumed unchanged upon excitation; the results in parentheses have been obtained using free-atom excitations between the (calculated) optimum ground and excited states.

Atom	Binding energy shift (eV)		
	Experiment [9]	Theory [33]	Present work
Ti	12.3	13.3	14.46 (9.30)
V	13.3	13.3	14.46 (8.90)
Co	14.0	17.0	15.62 (8.36)
Ni	15.2	17.2	14.75 (7.26)
Cu	7.3	8.7	6.44 (6.44)

In the present application, we are restricted to a much more approximate model calculation of the BESs of the inner electrons of an atom which occur as the atom passes from its free-atom state to the corresponding bulk one. In particular, we calculate the electronic BESs associated with the 2s electrons of bulk Ti, V, Co, Ni and Cu atoms; the BESs are given with respect to the electronic BEs of the corresponding free-atom state. For such inner-electron BESs, there exist some reported data [9, 33] which may be used for the necessary comparisons. These data are included in table 2 along with our results.

The experimental data listed in our table 2 have been taken from reference [9] while the theoretical ones have been obtained from the tabulation of Shirley *et al* [33]. The latter refer, on the one hand, to the free-atom relativistic Hartree–Fock–Slater type of calculation [36, 37] and include relaxation contributions to the BEs, but do not account for any differences in correlation energy between the two states involved in the excitation process; on the other hand, they refer to semi-empirical bulk-state calculations in which the effect of the solid-state environment is approximated by a Coulomb integral between the core level under consideration (in the present case this is the 2s core level) and a screening

orbital. Semi-empirical theoretical results for the electronic 2s BESs of bulk atoms, given relative to the free-atom state, have also been reported by Johansson and Martensson [9] who employed a Born–Haber cycle in order to describe the excitation process; their results are closer to the experimental data (listed in our table 2) than the results of Shirley and collaborators [33].

In obtaining our results, the BEs of the 2s state of the bulk atoms are obtained according to the procedure discussed above. In particular, we calculate the total energy of a metal system with one substitutional impurity, the latter being a crystal atom with a 2s-electron hole appropriately neutralized by an additional valence charge spread over the unit cell containing the excited atom. The 2s-electron BE of the bulk atom is, then, obtained by subtracting the total energy of the non-excited system from that of the excited one.

Our calculations of the BEs of the free atoms were performed using a standard LDA-based computer code compatible with our computer codes used for the bulk state calculations. In particular, our programs refer to non-magnetic cases and employ the Hedin–Lundqvist [38] expression for the exchange and correlation energy per atom [39]. However, our free-atom results suffer, as usual, from one inherent drawback, namely they do not always describe the experimentally found electronic configurations of the ground state of the free atoms. It is recalled that the experimentally observed ground state of Ti, V, Co and Ni is of the type $3d^n4s^2$, where $n = 2, 3, 7, 8$ respectively, and for the Cu atom it is of the form $3d^{10}4s^1$. In contrast, the LDA-based theoretically found [34] ground-state configurations are of the form $3d^{n+1}4s^1$, where $n = 2, 3, 7, 8, 9$ for Ti, V, Co, Ni and Cu respectively [41]. In other words, only for the free Cu atom is there unambiguous agreement between the results of the LDA theory and the experiment in the description of the electronic ground-state configuration. For this reason, in calculating the BEs of the free atoms in the present application, we have used the experimentally observed electronic configurations of the ground states of the free atoms and, additionally, we have assumed that these configurations do not change in the excited states. This assumption is not always correct, as a change in the valence electronic configuration of a free atom may occur upon excitation [41]. Nevertheless, and for reasons of completeness, we have also included in table 2 our results corresponding to free-atom transitions from the (calculated) optimum ground state to the (calculated) optimum excited state. As it is apparent from table 2, our results, which are based on the experimental ground state of the free atoms, are in very good agreement with the existing theoretical and experimental data [42]. In the case of Cu, for which the LDA predicts the experimentally observed ground and excited state for the free atom, the agreement is very satisfactory. However, our results based on the theoretically found ground and excited states of the free Ti, V, Co and Ni atoms exhibit pronounced differences when compared with other theoretical and experimental results [42]. The difference between these two sets of results indicates the source of our calculational error, which is the limitation of the free-atom calculations. At the same time, the results of table 2 make clear the underlying difficulties associated with the theoretical determination of the BESs of bulk atoms given with respect to the free-atom state. In addition to this, from our results one can explain why LDA is expected to be more successful in calculations involving differences in the BESs associated with various local environments of the bulk atoms (i.e. surface relative to bulk electronic BESs [35]). Our method is expected to be suitable for calculating surface BESs with respect to the BEs of the bulk state. On the other hand, it becomes clear that the accurate calculation of the BESs given with respect to the free-atom state requires more sophisticated calculational approaches which can, in a compatible way, match bulk and atomic computational techniques which go beyond the LDA approximation and its present improvements (e.g. the generalized gradient approximation).

It is understood that the calculation of the electronic BESs of core electrons is a very difficult computational task. Nowadays, improvements in the LDA theory promise improved accuracies in the calculation of the electronic BEs. Nevertheless, due to mutual cancellations of the errors that occur in the calculation of the electronic BEs, the LDA-based calculation of the BESs seems to lead to results in fair agreement with available experimental data, provided that the correct ground and excited atomic state are used. The present application demonstrates this fact as well. In addition to that, our results for Cu, for which the free-atom calculations are in agreement with experiment, also imply, as in the case of the charge-transfer calculations, that the contribution to the electronic BESs which comes from charge relaxation in the unit cells surrounding the excited atom is only a small percentage of the overall solid-state effect. This, in fact, supports the local character of the screening of the core hole which earlier theories [9, 33] attributed to the d electrons. In turn, this observation gives extra support to the underlying assumption of locality which is inherent in the approximate calculational method that is proposed here.

4. Conclusion

In conclusion, we have shown that localized perturbations (processes) in complex systems can be suitably simulated by local potential shifts superimposed on the single-electron potentials of the unperturbed systems. The utilization of this idea allows one to propose approximate calculational approaches and perform calculations for complex systems in an efficient computational way which can also help one to understand the underlying physics of the problems concerned. We have demonstrated this possibility by applying our ideas to two computationally demanding problems:

(i) the calculation of the charge transfer associated with a substitutional impurity in a metallic host; and

(ii) the calculation of inner-electron BESs associated with bulk atoms and given relative to the free-atom state.

In both cases, our proposed approximate calculational method gave results in good agreement with existing experimental and theoretical data.

The proposed new method does not aim to replace existing elaborate *ab initio* methods—especially in the case of single-impurity systems, for which there is no doubt that the proper way to treat them is to consider the impurity and several nearest-neighbour shells as an impurity cluster to be embedded in the host lattice (as for example is done in references [20–24] or in our level of approximation (iii)). This is, of course, a formidable calculation, and the computer time required to perform it increases as the cube of the number of atoms in the cluster. There are times when great precision may not be required for a given application, and it is interesting to note that there seems to be a much easier calculation that will give surprisingly good predictions as was demonstrated in the applications presented. The success of the present calculations allows us to consider the proposed method as a promising calculational scheme for studying complex systems.

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