Parameter-free calculation of $K\alpha$ chemical shifts for Al, Si, and Ge oxides

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The chemical shifts of the $K\alpha$ radiation line from Al, Si, and Ge ions between their elemental and oxide forms are calculated within the framework of density functional theory using ultrasoft pseudopotentials. It is demonstrated that this theoretical approach yields quantitatively accurate results for the systems investigated, provided that relaxations of the valence electrons upon the core-hole transition are properly accounted for. Therefore, such calculations provide a powerful tool for identification of impurity states based on x-ray fluorescence data. Results for an Al impurity implanted in silica are found to be in excellent agreement with experimental data, providing support for the proposed atomic geometry.

A crucial role of theory in the study of defects and impurities in solids is to provide a link between experimentally accesible information and atomic-scale models, thus facilitating the interpretation of experimental data. Therefore, it is of considerable importance to investigate the extent to which experimentally accessible quantities can be predicted directly from parameter-free electronic-structure calculations. Various types of core-level spectroscopies have been used successfully to probe the environment around specific elements in solids. The virtue of these techniques are that they are element-specific and in principle applicable to nearly all the elements in the periodic table. One method, which has been used extensively to determine chemical states of various impurities in silicates and other oxide hosts,[1–5] is x-ray fluorescence spectroscopy (XFS), which measures the radiation emitted from hole transitions between different core shells in the element of interest. Small shifts of the transition energies can be observed among different compounds, and these data can then be used to distinguish different chemical environments. Theoretical modeling using the Hartree-Fock-Slater approximation on small cluster models have reproduced the experimentally observed trends rather well, but the quantitative accuracy of the results is less satisfactory.[2–4] The question is then whether more elaborate schemes accounting for crystal structure can provide more accurate predictions. A number of studies within the framework of density functional theory[6,7] (DFT) have focused on the calculation of surface core-level shifts (SCLS), either by direct inspection of Kohn-Sham eigenvalues for core states (the so-called ''initial-state theory''[8–10]) or more elaborate approaches comparing total energies for the system with and without the core hole (commonly denoted ''final-state theory'').[9,11] Also in this case, experimental trends have been well reproduced, but with somewhat mixed results regarding the quantitative results for the energy shifts. Recently, Methfessel *et al.*[12] determined chemical shifts of the core-level binding energy (CLBE) for Mg $1s$ and Au $4f$ levels between the Mg-Au alloy and the elemental metals within both initial- and final-state theory, using an all-electron method. The latter yielded excellent results for the Au $4f$ shift, and a fairly small ($\sim$25%) deviation of the predicted Mg $1s$ shift compared to the experimental value. The purpose of the present paper is to investigate the accuracy of similar approaches to the cal-

culation of XFS data when implemented with ultrasoft pseudopotentials.[13,14] Although this approach to electronic-structure calculations only provides an indirect description of the core states, I shall demonstrate that the final-state theory is able to predict the chemical shifts observed in XFS between elemental Al, Si, Ge, and some of their oxide compounds to an accuracy of $\sim$10%, whereas more approximative approaches are found to yield poor results. Furthermore, I shall use the method to provide experimental support for an earlier proposed structure for Al implanted in silica.[15]

The chemical shift of core-level transition energies mainly derives from the spatial variation in the core region of the electrostatic potential arising from the valence electron density. A constant potential shift (e.g., the work function) has no influence on the transition energy, which is therefore a purely local probe of the chemical environment. However, the change in the core charge distribution upon the transition also affects the valence charge density, as the hole potential becomes more attractive with decreasing size of the hole orbital. Although the redistribution of valence charge upon core-core transitions is smaller than that which accompanies core-electron emission (in which the effective charge of the ion changes by e), the importance of this effect cannot *a priori* be excluded. In order to treat valence relaxations properly, I use a scheme similar to the final-state theory of SCLS: Two calculations are performed, with the hole present in either the initial- or final-state core orbital, and the resulting total energies are subtracted to get the transition energy. In the present work, the Perdew-Wang 1991 (PW91) approximation[16] to density functional theory[6,7] (DFT) is used, and the resulting Kohn-Sham equations are solved by means of a plane-wave expansion using Vanderbilt's ultrasoft pseudopotentials (US-PP's).[13,14] The close connection between this method, and the all-electron PAW scheme developed by Blöchl[17] has been carefully discussed by Kresse and Joubert.[18] These authors showed that Vanderbilt's theory can be viewed as a linearization of the PAW energy functional around the valence occupancies in the atomic calculation used to construct the pseudopotential. As the core-valence contribution to the electrostatic interaction energy is linear in the valence occupation numbers, this important contribution is treated correctly in the US-PP formalism. In the region of space where the density of core charge dominates

that of the valence charge, this will also be approximately true of the exchange-correlation (xc) interaction energy. The nonlinearities in the xc functional in regions where the core and valence densities are of comparable magnitude can usually be accounted for using the partial core correction of Louie, Froyen, and Cohen.[19] Thus, the errors due to the US-PP approach arise mainly from the change in valence-valence interaction energy within the pseudopotential construction spheres upon redistribution of valence charge. However, as the valence charge redistribution is quite small, we must expect this to be a minor effect (this does *not* mean that valence relaxation effects are unimportant, as they affect changes in the electrostatic potential seen by initial and final core states). Of course, the absolute transition energies between the core states cannot be calculated in the US-PP formalism. What results from the calculation is the contribution to the transition energy arising from core-valence interactions, but this is exactly what is needed in order to evaluate the chemical shifts.

In the present study I shall consider chemical shifts of the $K\alpha$ radiation line arising from $2p$ to $1s$ transitions in Al, Si, and Ge atoms in various environments. For each element in question, ultrasoft pseudopotentials based on atomic all-electron calculations with a hole in either the $2p$ or $1s$ orbitals are constructed. Now a supercell calculation is set up, in which one atom is described by the core-hole pseudopotential and the others by the usual neutral pseudopotentials. The total-energy difference between calculations with the hole in the $1s$ and $2p$ channels is then taken as a measure of the contribution to the transition energy from core-valence interactions. By comparing this energy difference in the various compounds of interest the chemical shifts are deduced. The electron number is taken to be equal to that in the neutral compound, i.e., the system under study will be charged due to the core holes. The resulting divergence of the Coulomb potential in a repeated-cell geometry is cancelled by addition of a uniform neutral background charge, as is commonly done. This approach introduces a total-energy error whose magnitude is difficult to estimate precisely, but whose leading term scales with the inverse Wigner-Seitz radius of the supercell applied.[20] From a theoretical point of view, it is therefore a benign feature of x-ray fluorescence that initial and final states of the same total charge are compared, as this will make most of the electrostatic error terms cancel out.

Calculations have been performed for the following substances: Si, Al, and Ge in their elemental crystalline form, SiO_2 and GeO_2 in their α-quartz and rutile modifications, and Al_2O_3 in the corundum structure. All calculations were done in the experimentally determined equilibrium geometries. The ultrasoft pseudopotentials were constructed with two projector functions in each sp channel, while in the d channel one projector function was used for Al and Ge and two for Si. The Ge $3d$ states were treated as core states in the calculations cited here. It was found that the inclusion of these states in the valence gave no difference in the resulting chemical shifts. The nonlinear core correction of Louie, Froyen, and Cohen[19] was applied in all cases, with pseudopotential construction sphere radii of 1.2 a.u. for Al, 1.0 a.u. for Si, and 1.5 a.u. for Ge. In the latter case, a calculation
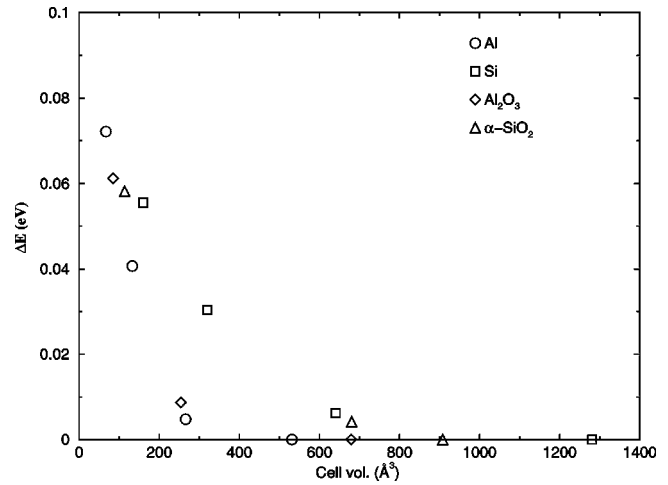

FIG. 1. Convergence of core-valence interaction energies for some Al and Si compounds as a function of supercell size. For each system, the results have been shifted such that the result from the largest supercell is at zero energy.

using pseudopotentials without the nonlinear core correction was found to decrease the $K\alpha$ chemical shift between elemental Ge and the α-quartz form of GeO_2 by $\sim 7\%$. The result obtained with the partial core correction probably provides the better approximation to the all-electron result. Plane-wave cutoffs for the wave-function expansions of 250 eV were used for all the elemental crystals and 340 eV for all oxides. The cutoff for expansion of pseudo-charge-densities was in all cases set at four times the wave-function cutoff. The elemental substances were studied in a bcc supercell containing 32 elementary unit cells. The **k**-point sampling was done using a $2\times2\times2$ Monkhorst-Pack grid for Si and Ge, and an $8\times8\times8$ grid for Al, which is the only metallic compound in the present study. For the oxide compounds, supercells were obtained by doubling the elementary Bravais lattice vectors in all directions, except in the case of the rutile structure, where the vector in the c direction was tripled and the others doubled. The Al_2O_3 supercell thus contains 80 atoms in total and the others 72. In order to check the dependence of the results on the size of the supercell, a series of calculations in cells of different size was performed. In Fig. 1 the results are shown as a function of cell volume. For each compound, the data have been shifted so that the result obtained in the largest cell is at zero energy. It can be seen that the choice of a sufficiently large supercell is quite important for attaining chemical accuracy. Based on the results presented I estimate the uncertainty deriving from the finite supercell size to be on the order of 0.01 eV.

The central results of the present paper are shown in Table I, where the $K\alpha$ chemical shifts derived from the calculated $1s$-$2p$ energy differences are compared to the experimental values. It can be seen that the difference between theoretical and experimental values is less than 10% for all crystals under consideration. This accuracy is sufficient to clearly distinguish different states of an element, such as the sixfold coordinated environment of the Si/Ge ions in the rutile oxide structures versus the fourfold coordination in the α-quartz structure. Therefore, the present theoretical ap-

TABLE I. Chemical shifts of $K\alpha$ radiation lines from Al, Si, and Ge. The shift X_mY_n/X denotes the chemical shift of X in the compound X_mY_n relative to elemental X. Units are eV. SiO_2:Al denotes silica implanted with Al ions.

System	Theory	Expt.
Al_2O_3 /Al	0.43	0.39 [a]; 0.41 [b]
SiO_2 :Al/Al	0.28	$\sim$0.29 [b]
α-SiO_2 /Si	0.72	0.66 [c]
Rutile SiO_2 /Si	0.88	0.80 [c]
α-GeO_2 /Ge	0.26	0.25 [d]
Rutile GeO_2 /Ge	0.33	0.32 [d]

[a]Reference 2. [c]Reference 4.
[b]Reference 5. [d]Reference 3.

proach constitutes a powerful tool for interpreting x-ray fluorescence data in terms of atomic geometries. As an example of such applications, I have applied the method to a geometry for an implanted Al impurity in silica, which was suggested in an earlier publication based on PW91 total-energy calculations.[15] In these calculations, the implanted Al impurity was found to substitute for an Si atom, which was displaced into the interstitial region, forming elongated bonds to two O atoms close to the Al ion. The structure was investigated in a 54-atom supercell. The resulting $K\alpha$ chemical shift is 0.28 eV. Fukumi and co-workers[5] measured chemical shifts of Al ions implanted in silica glass and found a range of values (some of them with rather large error bars) depending on implantation dose and anneal conditions. A value of $\sim$0.29 eV seems consistent with all the reported data points and error bars. This is in excellent agreement with the theoretical value.

The calculational procedure outlined above requires construction of two new pseudopotentials and subsequent determination of the self-consistent charge density in a supercell of sufficient size. It is of some interest to investigate the extent to which some of these steps may be avoided by using a more approximative approach. In the theory of SCLS good results can in some cases be obtained by using a simple first-order perturbation theory, in which the expectation value of the core-valence interaction in the core state of interest is taken as a measure of the chemical shift at a particular site.[10] To investigate the merits of similar approaches in the context of x-ray fluorescence, I construct an approximate all-electron charge density by augmenting the pseudo-wavefunctions with atomic orbitals as outlined in Ref. 21. The Hartree interaction energies between this density and the $1s,2p$ core orbital densities can then be calculated, and the difference provides a measure of the $K\alpha$ energy shift arising from core-valence interactions at the site in question. This approach neglects the effects of exchange and correlation between core and valence states, and the effects of relaxations in the valence electron density between different core configurations. In Table II results for the Si and Ge compounds are shown. The calculation has been performed both in the neutral state in which all core levels are occupied, and in the states with a hole present in either the $1s$ or $2p$ channels. The magnitude of the shifts is generally larger in the

TABLE II. Chemical shifts for the Si and Ge oxides in different approximations. PT-n denotes a first-order perturbation calculation, as described in the text, in the neutral configuration (all core states filled up). PT-$1s$ and PT-$2p$ denote a similar calculation with a hole in the $1s$ or $2p$ channels, respectively. Units are eV.

System	PT-n	PT-$1s$	PT-$2p$	Full theory
α-SiO_2 /Si	0.39	1.09	1.12	0.72
Rutile SiO_2 /Si	0.98	1.32	1.39	0.88
α-GeO_2 /Ge	0.15	0.31	0.31	0.26
Rutile GeO_2 /Ge	0.27	0.40	0.41	0.33

charged systems, which is understandable, since extra valence charge is attracted by the core holes, thus increasing the core-valence interactions. The valence charge densities close to the nucleus in the different core configurations are reported in Fig. 2 for elemental Si and Ge. It can be seen, that a substantial change in the charge-density profile occurs on going from a filled to a partially filled core shell, which is
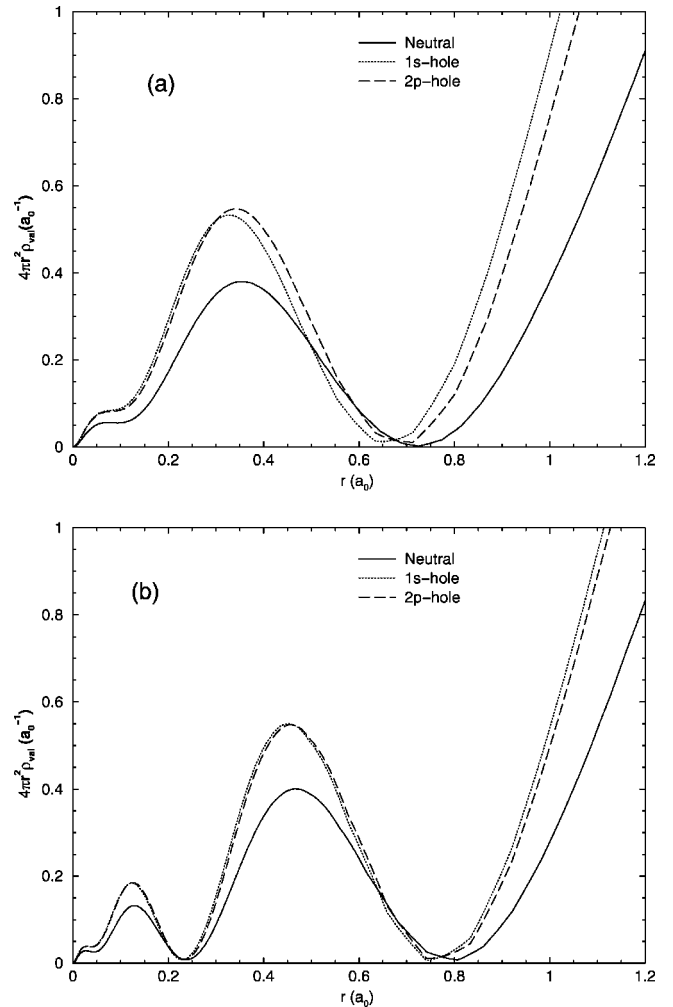

FIG. 2. Spherically averaged valence charge-density profile in elemental (a) Si and (b) Ge. Results are presented for the neutral configuration, with all core states filled, as well as for the states with a hole in either the $1s$ or $2p$ channel.

to be expected as the effective valency of the element is changed by 1. However, even between the $1s$ and $2p$ hole states there are noticeable differences in the charge distribution, especially for Si. As a consequence, the quantitative accuracy of the various perturbative approaches is not so good. The calculations in the charged configurations seem to reproduce the relative magnitudes of the shifts fairly well, and the general overestimate of the shifts might be reduced by proper inclusion of exchange-correlation effects. On the other hand, from a computational point of view, the theory based on the neutral configuration is the most interesting, as it eliminates the need for supercells and core-hole pseudopotentials. Unfortunately, although the experimental trends are still reproduced, this theory provides poor quantitative accuracy, both in terms of absolute and relative shifts. It must be

concluded that a proper account of charge relaxation effects is essential for obtaining accurate predictions of the chemical shifts. A similar finding in the case of CLBE calculations was reported by Methfessel et al.[12]

In conclusion, I have shown that density functional theory, within the PW91 approximation, contains the essential physics needed to predict chemical shifts of the $K\alpha$ radiation line in various oxidation states of Al, Si, and Ge, provided that relaxations of the valence electron states between the different core configurations are properly accounted for. Furthermore, comparison of theoretical calculations and experimental $K\alpha$ line data support an earlier proposed structural model for an Al atom implanted in silica.

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