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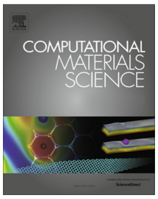

Multi-reference extension to virtual crystal approximation pseudo-potentials

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ABSTRACT

In this study a computational method of the multi-reference VCA (virtual crystal approximation) pseudo-potential generation is presented. This is an extension of that proposed by Ramer and Rappe (2000), the scheme of which is in want of the explicit incorporation of semi-core states. To compensate this drawback, a kind of fine tuning is applied to the non-multi-reference VCA pseudo-potential; the form of the pseudo-potential is slightly modified within the cut-off radius in order that the agreements between the pseudo-potential and all-electron calculations are guaranteed both for semi-core and valence states. The improvement in the present work is validated by atomic and crystalline test calculations for the transferability and the lattice constant estimation.

1. Introduction

The purpose of the present article is to show a way to generate a reliable pseudo-potential which is applicable to inhomogeneous or super-lattice crystal structures.

Frozen core model in pseudo-potential generation often suffers from a kind of inaccuracy where the relaxation in the semi-core state is not negligible, as is notable in transition metals, since, in these elements, owing to the overlapping of the semi-core and the valence states, it is inappropriate to assume the semi-core state as chemically inert one. In these elements, for the more accuracy, the pseudo-potential is generated for the topmost, fully-occupied, semi-core p level, not for the empty valence state. This treatment allows the relaxation of the semi-core state in the simulation, but causes an inevitable inaccuracy in the pseudo-potential result. In the atomic pseudo-potential computation, the semi-core state, lying in the lowest p-level, is in exact agreement with the all-electron result as to the energy and the square norm of the amplitudes of the wave-functions outside the cut-off radius. On the other hand, there is no such an agreement for the empty valence p-level, obtained as the second-lowest p-level, in which the discrepancy between the pseudo-potential and the all-electron computations always exists. In order to correct this drawback, it is necessary to introduce some schemes called multi-reference-pseudo-potential (MRPP) [1], so that the calculated properties for the valence and semi-core states by the pseudo-potential and all-electron computation coincide with each other. (In some references, this technique is described as “the explicit incorporation of semi-core states”.)

Concerning the crystalline pseudo-potential computation, there is an approximating method named “virtual crystal approximation (VCA)”. This is a method to deal with the disordered crystal (and also applicable to the super-lattice structure). To represent the inhomogeneity and to reproduce the averaged property of the disordered crystal, the atomic potentials are, in some ways, mixed in accordance with the composition ratio of the atomic replacement. In the simplest implementation, the pseudo-potential for randomly distributed elements A and B is simply averaged by the composition ratio as $x \times V_A + (1 - x) \times V_B$. This approximation is not reliable in some cases. Meanwhile, there are more refined ways in VCA; of which the Ramer–Rappe method [2] is the most reliable one; it attains more quantitative crystalline simulations than the simply averaged VCA does. The success of this method will be ascribed to its ability, by which the eigenvalue and the charge distribution of the single atom in VCA model can be adjusted to the averaged all-electron computation in accordance with the composition ratio. However, it still lacks the explicit incorporation of semi-core states.

Touching these two topics, the present work proposes a method to generate multi-reference crystal VCA pseudo-potential. This is an extension to Ramer–Rappe scheme, toward which a kind of fine-tuning is applied so that the multi-reference accuracy, i.e., the explicit incorporation of semi-core states could be achieved.

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2. Computational method

In the following, these notations are used; the two elements to be averaged by VCA are denoted by $A(B)$; the principal and angular quantum numbers are denoted by $n(n')$ and l; the wave-functions, eigenvalues and the potentials are denoted as $\phi^{A(B)}_{n(n'),l}(r)$, $\varepsilon^{A(B)}_{n(n'),l}$ and $V_{A(B)}(r)$. The composition ratio is denoted as α for element A and β for B.

The wave-functions in the virtual atom (i.e. the averaged image of randomly distributed two elements A and B in the equivalent atomic site) are computed under following conditions.

[I] The averaged nuclear potential ($\alpha + \beta = 1$ here):

$$V^{VCA}_{nuc}(r) = \alpha V^{A}_{nuc}(r) + \beta V^{B}_{nuc}(r) = \frac{-(\alpha Z^{A}_{nuc} + \beta Z^{B}_{nuc})}{r}. \tag{1}$$

[II] The averaged eigenvalue (for the lowest eigenstate):

$$\varepsilon^{VCA}_{1,l} = \alpha\varepsilon^{A}_{n,l} + \beta\varepsilon^{B}_{n',l}. \tag{2}$$

[III] The boundary condition towards the infinity:

$$\phi^{VCA}_{1,l}(r) \to 0 \quad \text{as} \quad r \to 0. \tag{3}$$

[IV] The norm conserving condition:

$$\int_{r_c}^{\infty} \left|\phi^{VCA}_{1,l}(r)\right|^2 r^2 dr = \alpha \int_{r_c}^{\infty} \left|\phi^{A}_{n,l}(r)\right|^2 r^2 dr + \beta \int_{r_c}^{\infty} \left|\phi^{B}_{n',l}(r)\right|^2 r^2 dr. \tag{4}$$

[V] The averaged core charge:

$$\rho_{core}(r) = \alpha\,\rho^{A}_{core}(r) + \beta\,\rho^{B}_{core}(r). \tag{5}$$

The computation proceeds as follows.

(1) With the given energy $\varepsilon^{AVG}_{1,l}$, the node-less numerical solution $\phi^{VCA}_{1,l}(r)$ of the atomic wave equation is calculated by an inward integration from the infinity to the cut-off radius r_c. The potential is determined by the conditions of [I] and [V]. The wave-function between the cut-off radius and the infinity is normalized so that the condition [IV] is satisfied.

(2) Prepare the complete pseudo-wave-function. For this purpose, $\phi^{VCA}_{1,l}(r)$ is extended toward the origin ($r = 0$) by some analytic function. The pseudo-charge and the electronic potentials are computed now.

(3) Iterate (1) and (2) and obtain the self-consistent charge. The new valence charge density is then computed from the valence pseudo-orbitals, so that the cycle should be completed. The cycle is repeated until the input and output of the pseudo-orbitals are equal. In the present implementation, it requires at most ten iterations, by the usual Anderson mixing, to gain the convergence of the self-consistent charge. Indeed, the self-consistent calculation appears to be superfluous. In the usual pseudo potential generation, pseudo-orbitals are uniquely determined without self-consistent calculation, if the all-electron potential, the energy spectrum, and the norm-conservation conditions are fixed. Nevertheless, the requirement of the self-consistency is a special feature in the pseudo-potential generation by the Grinberg-Ramer–Rappe scheme [3] and its variants. This is required to construct a scalar-relativistic pseudo-potential that provides exact agreement with relativistic Dirac-Slater all-electron eigenvalues at the reference configuration. The relativistic all-electron eigenvalues and the aggregate norm-conserving conditions are used to obtain the non-relativistic wave functions and potentials in the all-electron level as the self-consistent solution. This method improves transferability of the resulting pseudo-potential. (The down- and up-spin components in the relativistic equations are mixed with each other in order to construct the valence charge, which should be reproduced by the non-relativistic Schrodinger equation by means of the pseudo-potentials, with the agreement of the valence charge eigenvalues. This request has an analogy to the problem of the VCA pseudo-potential generations.) Since the present method is one of the variants of the Grinberg–Ramer–Rappe scheme, and in order to make allowance to accurate relativistic extension, the VCA pseudo potential generation algorism presented here follows that of Ramer and Rappe, which constructs self-consistent charge in the iterated cycles.

(4) Determine the VCA pseudo-potential which generates $\phi^{VCA}_{1,l}(r)$.

(5) Apply the fine tuning to realize the multi-reference. This step follows Teter's method to generate an extended type of the norm conserving pseudo-potential [4]. In this method, the self consistent potential $V_{scf}(r)$ is modified near the origin by means of the cut-off function $h(r)$ and the augmentation terms $\sum_{i=1}^{n} a_i g_i(r)$. The coefficients a_i are adjustable ones so that the computed result will take the required value. (It is noted here that the extended pseudo-potential by Teter is, in origin, not the approach to explicit incorporation of semi-core states. Its purpose is to improve the transferable property of the pseudo-potential by keeping the agreement of the "chemical-hardness" between the pseudo-potential and all-electron computation.)

In the present VCA case for multi-reference extension, following conditions should be satisfied: the eigenvalue and the square norm outside the cut-off radius of the second lowest orbital $\phi^{VCA}_{2,l}(r)$ agree with the averaged all-electron result. These conditions are given as

$$\varepsilon^{AVG}_{2,l} = \alpha\,\varepsilon^{A}_{n+1,l} + \beta\,\varepsilon^{B}_{n'+1,l}, \tag{6}$$

and

$$\int_{r_c}^{\infty} \left|\phi^{VCA}_{2,l}(r)\right|^2 r^2 dr = \alpha \int_{r_c}^{\infty} \left|\phi^{A}_{n+1,l}(r)\right|^2 r^2 dr + \beta \int_{r_c}^{\infty} \left|\phi^{B}_{n'+1,l}(r)\right|^2 r^2 dr. \tag{7}$$

The computational steps from (1) to (4) are the same as those in the original Ramer–Rappe method; the step at (5) is the essential extension by the present work. In this step, the fine tuning proceeds in the following way. The conditions to be satisfied are newly given as:

[I′] The pseudo-potential is readjusted from the screened VCA pseudo-potential by means of above cut-off functions and coefficients. In the implementation of the present work, the functional form is given as

$$V^{MRPP}_{l,ps}(r) = \sum_{i=1}^{n} a_i g_i(r) + h(r/r_c)\,V^{VCA}_{l,ps}(r) + c_l(1 - h(r/r_c)), \tag{8}$$

where $h(r)$ is a cut-off function which is zero at the origin and becomes unity out of the cut-off radius. $g_i(r)$ are functions having *i–1* nodes, which are unity at the origin and go to zero with the zero slope at the cut-off radius. This is an extension of the functional form of the provisional pseudo-potential in