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Bond-Order Potentials with Analytic Environment-Dependent Tight-Binding Integrals: Application to BCC Molybdenum

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ABSTRACT

We present a new Screened Bond-Order Potential (SBOP) for molybdenum in which the environmental dependence of two-center tight-binding bond integrals has been implemented via a recently developed analytic expression. These bond integrals reproduce very well the numerical ab-intio values of screened LMTO bond integrals. In particular, they display the large discontinuity in ddπ between the first and second nearest neighbor of the bcc lattice whereas they do not show any discontinuity in ddσ. This dependence can be traced directly to the angular character of the analytic screening function and is shown to be critical for the behavior of the second nearest neighbor force constants. The new BOP eliminates the problem of the very soft T2 phonon mode at the N point that is found in most two-center tight-binding models. Preliminary study of the core structure of 1/2<111> screw dislocations performed using SBOP indicates that the core is narrower and less asymmetric than structures found in previous studies, in agreement with recent ab-initio calculations.

INTRODUCTION

Tight-binding (TB) methods are a reliable approach for determination of total energies for materials in which covalent character of bonding plays an important role [1]. They comprise fundamental quantum mechanics, ensuring correct account of the angular character of bonds [2]. Atomistic calculations employing these methods are fast enough to treat systems of particles that are much larger than those attainable in ab-initio DFT based calculations. In recent years the tight-binding method with the orthogonal basis and two-center bond (hopping) integrals has been reformulated in terms of Bond-Order Potentials (BOP) [3]. This linear scaling TB scheme does not require use of periodic boundary conditions and all the calculations are performed in the real space. This is particularly expedient for studies of extended crystal defects, such as dislocations.

The key point in all TB schemes is to develop a suitable parametrization, which not only reproduces experimental and theoretical data for ideal lattice structures, but is transferable to configurations not included in the fitting. This is especially important when the method is to be used in studies of extended defects with structures very different from that of ideal lattices. However, this is a daunting task considering approximations and simplifications implicit in the TB scheme. One of the crucial approximations, embodied in the two-center orthogonal TB method, is the assumption of orthogonality of the underlying basis set. This, of course, can never be exact since the atomic-like orbitals centered at different sites overlap. Several studies have shown that the effects of non-orthogonality can be to a good approximation accounted for by environmental dependence of the two-center TB parameters [4, 5]. For this reason a new

screened bond-order potential (SBOP) formalism, which includes non-orthogonality via analytic concept of a screening function, has recently been developed [6].

In this paper we present a first application of this scheme for the case of molybdenum for which it has been found that the transferability of the unscreened bond integrals is limited. The unscreened BOP potentials were quite successfully employed in modeling of both pure transition metals [7, 8] and certain alloys, such as TiAl [9]. However, several problems have been encountered, in particular for molybdenum. Specifically, in some parts the calculated phonon spectra deviate significantly from the experimental observations; the acoustic phonons near the N point are too soft. Furthermore, the vacancy formation energy was generally found to be too low. We will demonstrate in this paper that the new scheme is able to remedy these problems and thus provide even more reliable predictions for complex configurations of atoms.

In the following section we briefly summarize the introduction of the screening function, **S**, into the BOP scheme. We than demonstrate improvements of predicted properties of molybdenum within the screened model (SBOP). Finally, we present calculations of γ-surfaces and atomic structures of the 1/2<111> screw dislocation, which we compare with previous studies employing central-force potentials as well as with recent ab-initio calculations.

THEORY

The derivation of the SBOP formalism starts from the non-orthogonal two-center TB representation, whose secular equation is given as

$$\left[\mathbf{H}-\varepsilon_n(\mathbf{I}+\mathbf{O})\right]=0 \tag{1}$$

where **H** and **O** are the Hamiltonian and overlap matrices, respectively; **I** is the unit matrix. The intersite elements of the Hamiltonian matrix are given as usually in terms of the radial bond integrals and Slater-Koster angular functions. The elements of the screening function $\mathbf{S}=(\mathbf{I}+\mathbf{O})^{-1}$ can be obtained analytically using the same formalism as that employed in the original BOP theory [3]. Analytical expression for the elements of the screening function $S^{ij}_{\ell\ell'\tau}$ for an orbital $\ell\ell'\tau$ (ℓ, ℓ' = s, p, d; τ = σ, π, δ) between atoms i and j, can be obtained by inverting $(\mathbf{I}+\mathbf{O})$ using Green's function method and Lanczos recursion [10] up to the third level [6]. This function reflects the fact that the two-center bond integral between atoms i and j is altered due to the environment of the i-j bond, so that its screened value is given as

$$\widehat{\beta}^{ij}_{\ell\ell'\tau}=\beta^{ij}_{\ell\ell'\tau}(R_{ij})(1-S^{ij}_{\ell\ell'\tau}) \tag{2}$$

where $\beta^{ij}_{\ell\ell'\tau}$ is the corresponding unscreened bond integral. The screening function can be expressed in terms of second and third moments, μ_2 and μ_3, of the overlap matrix **O**, interference contribution c_I, defined in [6], and elements of the overlap matrix, $O_{\ell\ell'\tau}$, namely

$$S^{ij}_{\ell\ell'\tau}=\frac{(c^{ij}_1)_{\ell\ell'\tau}-(\overline{\mu}_2)_{\ell\ell'\tau}+(\overline{\mu}_3)_{\ell\ell'\tau}}{1+O^2_{\ell\ell'\tau}(R_{ij})-2(\overline{\mu}_2)_{\ell\ell'\tau}+(\overline{\mu}_3)_{\ell\ell'\tau}} \tag{3}$$

This formula has been derived in [6] assuming that the screening is due to the s valence electrons only, and is exact up to three-member rings of s valent atoms; the screening by more localized p and d valence electrons is much weaker.

In order to increase computational efficacy, we have employed a simplified version of the formula (3) in our calculations. Since the third moment and $O^2_{\ell\ell'\tau}$ are both very small they can be neglected in the denominator. The simplified formula for the screening function is then

$$S^{ij}_{\ell\ell'\tau} = \left[(c^{ij}_1)_{\ell\ell'\tau} - (\bar{\mu}_2)_{\ell\ell'\tau}\right] \Big/ \left[1 - 2(\bar{\mu}_2)_{\ell\ell'\tau}\right] \qquad (4)$$

Both c_1 and μ_2 are functions of overlap and bond integrals between atoms i, j and their neighbors as well as of angular functions of Slater-Koster type which depend on mutual positions of atoms and orbital types. Hence, this concept of screening function introduces into the BOP scheme only a small number of additional parameters. Specifically, these are dsσ interactions and the overlap integrals; the latter have the same scaling dependence as the corresponding bond integrals albeit a different magnitude. All these parameters can be extracted by analyzing ab-initio calculations and are not fitted to any particular physical property.

Figure 1 shows a comparison of ddσ and ddπ bond integrals in bcc molybdenum calculated by three methods: The BOP with unscreened bond integrals, new SBOP and ab-initio screened LMTO method. We do not present ddδ bond integrals since their behavior is analogous to that of ddπ bond integrals. The important feature of SBOP is its ability to reproduce the values of ddπ for the second nearest neighbors that, unlike ddσ, are environment dependent. As shown in the following section, this is crucial for certain phonon modes.
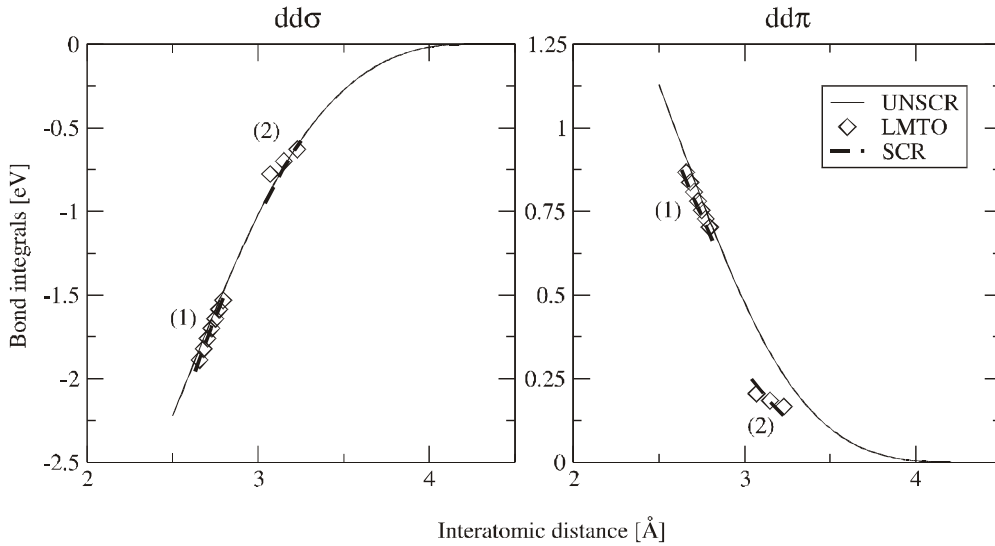

Figure 1. *ddσ and ddπ bond integrals for molybdenum: Full curves: analytical unscreened BOP; Dashed curves: SBOP; Symbols*: *Ab-initio screened LMTO. (1) and (2) label first and second nearest neighbors of the bcc structure, respectively.*

The SBOP differs from the original BOP only by addition of the screening function and, therefore, fitting of other parts of the potential is done in the same way as in the unscreened case [7]. The remaining repulsive contributions, which represent electrostatic and orbital-orbital interactions, are fitted to reproduce the basic properties of the ground state structure (lattice parameter, cohesive energy, elastic constants). Forces due to the bond part can be calculated using Hellmann-Feynman theorem provided the bond order is computed sufficiently accurately. The repulsive parts are given as analytical functions of distance between atoms and their differentiation is, therefore, straightforward.

RESULTS

We have constructed the SBOP for molybdenum and here we present a brief compilation of results documenting the validity and importance of the implemented screening concept. After constructing the potentials we have performed several tests contrasting SBOP calculations with ab-initio LDF based calculations. Specifically, comparison of energies of competing structures and calculations of deformation paths [7, 8]. In all cases the introduction of screening led to the improvement of the agreement between the two types of calculations. An exception is the A15 structure the energy of which calculated using SBOP deviates from that calculated ab-initio more than in the unscreened case. We believe that this is caused by dependence of unscreened two-center bond integral, $\beta_{\ell\ell'\tau}^{ij}$ in (2), on the local atomic density or effective coordination about the bond. Details of these tests and values of the potential parameters will be published elsewhere.

The vacancy formation energy was calculated using both the unscreened BOP and SBOP. The results are 2.3eV and 2.6eV, respectively. The experimental and ab-initio calculated values range from 2.9 to 3.1eV. It is apparent that SBOP leads to a more accurate value than the unscreened BOP.

However, a major problem encountered in previous studies was a too soft T2 phonon mode close to the zone boundary in the [110] direction, the N-point phonon [8]. This problem is common to all TB methods and can be traced to the behavior of the second nearest neighbor force constants. When screening is included, the energy associated with the ddπ bond integral at second nearest neighbors is decreased, in accordance with results of ab-initio calculations, and the frequency of the T2 mode of the N-point phonon increases. This is seen in Fig. 2, which demonstrates that this increase is more than three-fold. It is further seen from Fig. 2 that changes of the remaining two modes, while not so dramatic, are in the correct directions, towards experimental values.
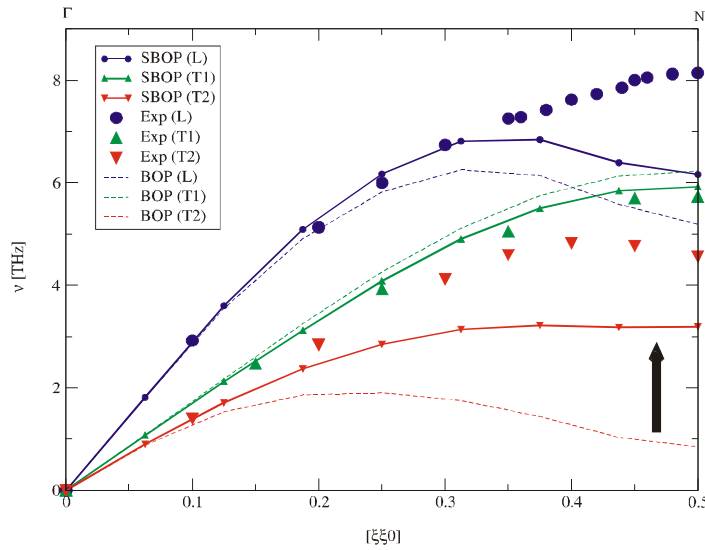

Figure 2*. Improvements in the phonon spectra of molybdenum for [110] direction. Full lines with symbols show the new SBOP results, dashed lines correspond to unscreened BOP and filled symbols are experimental date. The arrow shows the major improvement in the T2 mode.*

It has been generally accepted that the plastic behavior of bcc metals is governed by the special properties of 1/2<111> screw dislocations, in particular by their non-planar core structure

[11, 12]. A number of atomistic studies employing central-force potentials have, indeed, revealed structures, spread into three {110} planes of the <111> zone [11, 13]; similar results were obtained in calculations that included the directional covalent character of bonding in bcc transition elements [14].

As a prelude to dislocation simulations, we have investigated the γ-surface for the {110} slip plane which provides some insight into the shape and extension of the dislocation cores [12]. The contour plot of the {110} γ-surface for molybdenum calculated by SBOP is shown in Fig. 3a. Qualitatively, its shape is similar to that obtained for the unscreened BOP [8] but the maximum energy is about 40% higher and thus the surface is generally steeper. This suggests a narrower core since spreading of the dislocation into {110} plane becomes energetically less favorable.

As shown in previous studies [13], cores of screw dislocations in bcc transition metals always spread into three {110} planes but may possess either a three-fold or a six-fold symmetry. In the case of molybdenum studies employing central force potentials [13] as well as MGPT potentials including directional bonding [14] suggest the core with the three-fold symmetry. However, recent calculations employing ab-initio LDF based methods suggest cores with six-fold [15] or almost six-fold symmetry [16]. The differential displacement map [12] of the core structure calculated the present SBOP is shown in Fig 3b. This core displays three-fold symmetry but is much narrower and closer to the six-fold symmetry than the cores found in studies employing central force and MGPT potentials [14, 13]. This reflects, of course, the steepness of the γ-surface mentioned above. However, more importantly, this structure is close to that found in ab-initio calculations of Rao and Woodward [16] indicating again that the SBOP represents very correctly the bonding in molybdenum even in the highly distorted structures. Notwithstanding, the present calculations are only preliminary. They have been made using a relatively small block containing only 200 relaxed atoms and 500 atoms in the border region which interact with the relaxed atoms. Furthermore, investigation of the consequences of the core structure for plastic deformation requires detailed study of the effect of applied stresses on the core and eventual dislocation motion, similarly as it was done using central-force potentials [17, 18]. These studies are presently in progress.
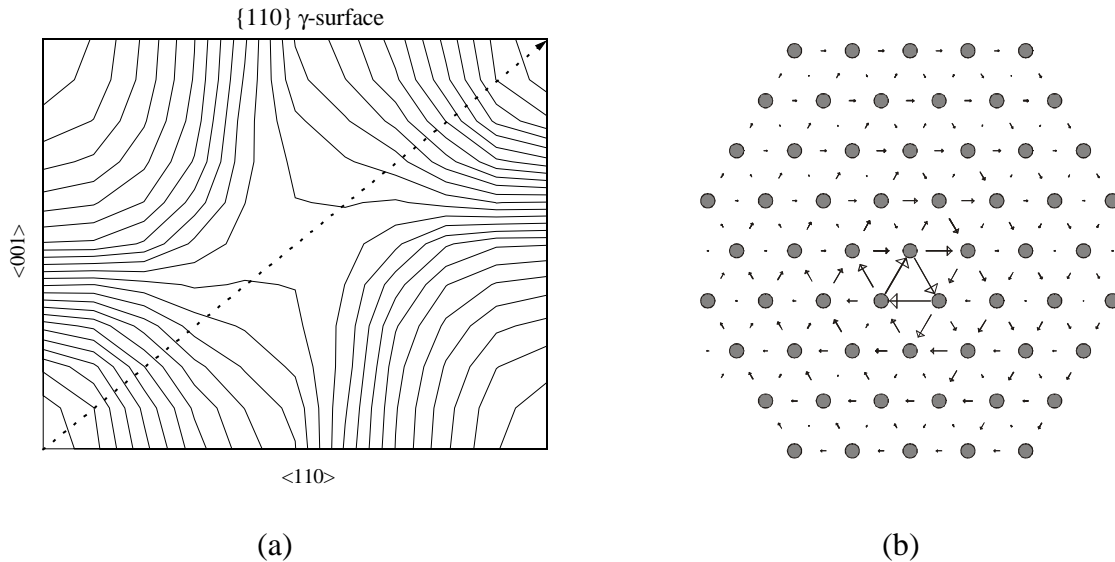

(a)   (b)

Figure 3. *(a) Contour plot of {110} γ-surface for molybdenum; the diagonal arrow is pointing in the [111] direction. (b) Core structure of the 1/2<111>screw dislocation in Mo; arrows show mutual displacement of atoms parallel to the dislocation line.*

CONCLUSIONS

We have demonstrated that the recently developed concept of screening of bond integrals which results in their environmental dependence [6] substantially improves their transferability. Constructed SBOP for molybdenum then predict much less soft T2 phonon in the [110] direction than the unscreened model and give vacancy formation energies closer to the experimental values. Results of screw dislocation core calculations are close to those found in recent ab-initio studies and while they are not principally different than those obtained using simpler schemes, they suggest appreciably narrower and less asymmetric cores. However, the implication for the glide of screw dislocations requires study of the effect of applied loads that are presently in progress.

ACKNOWLEDGMENTS

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