Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 329–333 (2004) 1151–1155

journal of nuclear materials

www.elsevier.com/locate/jnucmat

‘Quantum core’ interatomic potentials for transition metals

S.L. Dudarev *

EURATOM/UKAEA Fusion Association, Culham Science Centre, Oxfordshire OX14 3DB, UK

Abstract

Using tight-binding formalism, we derive a new expression for the energy of interaction between transition metal atoms. We show that angular interatomic forces result from the environment-dependent splitting of multiplets of degenerate d-states.

---

1. Introduction

Body-centred cubic transition metals and their alloys are prime candidate materials for fusion power plants, and the problem of deriving interatomic interaction potentials for transition metal atoms has recently attracted considerable attention in the field of fusion materials modelling [1,2]. This interest stems from the fact that in order to simulate collision cascades generated by 14.1 MeV fusion neutrons, as well as to study diffusion of defects generated by irradiation, it is necessary to be able to treat systems containing several million atoms. Systems of this size are well beyond the scope of currently available density functional or tight-binding electronic structure-based methods [3–6].

Most molecular dynamics studies of collision cascades performed so far were carried out using the Finnis–Sinclair potentials [7–9]. The energy of interaction between atoms in the Finnis–Sinclair model has the form

$$E_{\text{tot}} = -\sum_{\alpha} f\left(\sum_{\beta\neq\alpha}\rho(R_{\alpha\beta})\right) + \frac{1}{2}\sum_{\alpha\neq\beta} V(R_{\alpha\beta}), \qquad (1)$$

where the first term describes the attractive part of the potential, the second term represents pairwise repulsion, and $R_{\alpha\beta}$ is the distance between atoms α and β. The function $f(x)$ in the Finnis–Sinclair model is chosen in the form $f(x) = \sqrt{x}$, which is related to the functional form of the expression for the total energy derived using the second moment approximation in the scalar recursion expansion for the diagonal elements of the tight-binding Green’s function in the on-site representation [10].

The relatively simple functional form of Eq. (1) still leaves considerable freedom in the choice of functions $\rho(x)$ and $V(x)$. For example, the recent re-parameterisation by Han et al. [1] of an earlier version of the Finnis–Sinclair potential for vanadium has shown that, by altering the shape of functions $\rho(x)$ and $V(x)$ in comparison with the original parameterisation [8], it is possible to bring the energy of formation of several configurations of single interstitial atom defects into agreement with density functional calculations [5].

In this paper we investigate a different and previously unexplored route towards deriving a *directional* interatomic potential describing interaction between atoms in a transition metal. Similarly to the Finnis–Sinclair model, our method is based on the second moment approximation and takes into account virtual hopping paths of length two, originating from and coming back to the same atom. The significant difference between the formulation given below and the Finnis–Sinclair model is that we now take into account the fact that the starting group of d-states is degenerate and therefore the treatment of hopping of electrons requires using the *matrix* recursion rather than the *scalar* recursion approach.

Past applications of the matrix recursion method [11,12] only addressed the case of a half-filled d-band.

---

[*] Tel.: +44-1235 466513; fax: +44-1235 466435.

E-mail address: sergei.dudarev@ukaea.org.uk (S.L. Dudarev).

0022-3115/$ - see front matter Crown Copyright © 2004 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.271

This is illustrated, for example, by the use of the trace operator in Eq. (4) of Ref. [11]. In the case of a half-filled band the difference between energies evaluated using the matrix and the scalar recursion approaches is negligible (this stems from the fact that splitting of a multiplet of degenerate states does not affect the position of the centre of gravity of the multiplet). The conclusion about the relative insignificance of effects associated with the matrix character of the potential [11,12] may not therefore be applicable to the case where the average number N_d of d-electrons per atom differs from $N_d = 5$.

Below we generalize the Finnis–Sinclair model to the case of arbitrary filling of the d-band and show how this gives rise to a quantum correction to the energy of interaction between atoms in the core region of the Finnis–Sinclair potential. We also discuss the implications of the new approach for the treatment of interstitial defects in body-centred cubic vanadium.

2. Formalism

In this section, using tight-binding formalism, we attempt to derive the simplest possible functional form of the many-body short-range potential describing interaction between atoms in a transition metal and going beyond the Finnis–Sinclair model (1). If the atomic states associated with interacting atoms in a metal are degenerate, the initial system of atomic wave functions (in our case, the system of five d-orbitals localised on a given atom) representing the starting point for the recursion treatment of formation of interatomic bonds must be chosen in such a way that the change in them under the action of a small applied perturbation is small [13]. The second-moment expression for the matrix Green's function has the form [14,15]

$$(0|\widehat{G}(E)|0) = \frac{1}{(E+\mathrm{i}\epsilon)\widehat{I} - \frac{1}{E+\mathrm{i}\epsilon}(0|\widehat{H}^2|0)} \tag{2}$$

where $|0)$ is the subspace of five d-orbitals localised on a given transition metal atom, and $\widehat{H}$ is the short-range tight-binding Hamiltonian.

Fig. 1 illustrates the significance of direct overlap between d-orbitals in the case of interstitial atom defects. Interatomic bonds in the centre of an interstitial defect are strongly compressed (the effective degree of volume compression exceeds 35% [16]) and the directionality of d–d interactions should be expected to play a more significant part in the centre of the defect than in the less distorted regions of the material.

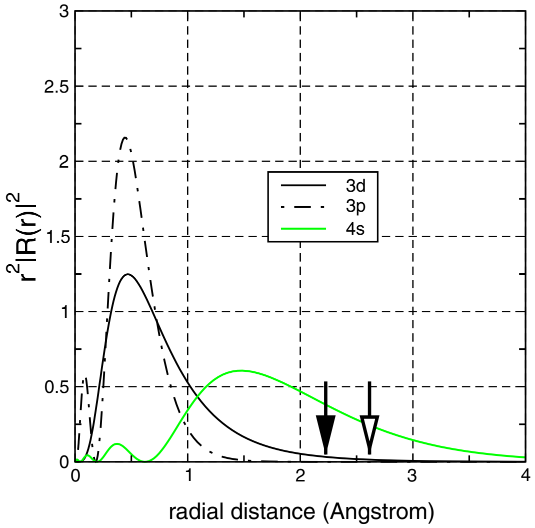

Fig. 1. Radial probability distributions of 3p, 3d and 4s states calculated for a vanadium atom using density functional theory in the local density approximation. The function $R(r)$ represents the radial part of the solution of the Schrödinger equation $\psi(\mathbf{r})$ where $\psi(\mathbf{r}) = R(r)Y(\theta,\phi)$. This function is normalised by the condition $\int_0^\infty r^2|R(r)|^2 dr = 1$. The black arrow indicates the distance ($r \approx 2.3$ Å) between the two nearest atoms in the centre of a $\langle 111\rangle$ single interstitial atom defect. The white arrow indicates the shortest distance ($r \approx 2.62$ Å) between atoms in bcc vanadium.

The dependence of the matrix elements of the Hamiltonian on the direction of the bond linking the interacting atoms is given by the Slater–Koster equations [17]. To find the elements of the 5×5 matrix $(0|\widehat{H}^2|0)$ entering Eq. (2), for each element we need to perform a summation over sets of five orbitals η centred on neighbouring atoms, for example,

$$(0|\widehat{H}^2|0)_{zx,zx} = \sum_{\eta,\mathrm{nei}} \langle zx,0|\widehat{H}|\eta,\mathrm{nei}\rangle\langle \eta,\mathrm{nei}|\widehat{H}|0,zx\rangle, \tag{3}$$

where η denotes the type of a d-orbital $\eta = \{xy, zx, yz, x^2-y^2, 3z^2-r^2\}$ centred on atom nei. To simplify the fairly lengthy expressions resulting from Eq. (3) we follow the convention that hopping integrals (ddσ), (ddπ) and (ddδ) scale as 2:−1:0. In this case we are left with only one independent function (ddσ) that determines the radial dependence of the bonding part of the potential, namely

$$(0|\widehat{H}^2|0)_{ij} = (\mathrm{dd}\sigma)^2 \mathscr{D}^2_{ij}(\theta,\phi). \tag{4}$$

The angular part $\mathscr{D}^2_{ij}(\theta,\phi)$ of the matrix $(0|\widehat{H}^2|0)$ is represented by the fifteen independent functions listed in Appendix A. By averaging $\mathscr{D}^2_{ij}(\theta,\phi)$ over the polar and azimuthal angles we find that

$$\frac{1}{4\pi}\int \sin\theta\, \mathrm{d}\theta \int \mathrm{d}\phi\, \mathscr{D}^2_{ij}(\theta,\phi) = \frac{3}{10}\delta_{ij}, \tag{5}$$

where δ_{ij} is the Kronecker delta symbol. In the limit where the matrix $(0|\widehat{H}^2|0)$ entering the expression for the Green's function (2) is described by Eq. (5) the denominator of Eq. (2) has two five-fold degenerate roots. However, if the full angular character of the matrix elements $\mathscr{D}^2_{ij}(\theta,\phi)$ is retained, the denominator of expression (2) has ten distinct non-degenerate roots.

3. The quantum core potential

In the limit where the angular part of the matrix $(0|\widehat{H}^2|0)_{ij}$ is approximated by expression $(0|\widehat{H}^2|0)_{ij} = (3/10)(\mathrm{dd}\sigma)^2\delta_{ij}$ that follows from (5), the effective interaction potential acquires the Finnis–Sinclair form. In this case the density of states associated with the Green's function (2) is given by

$$-\frac{1}{\pi}\Im(0|\widehat{G}(E)|0) = \frac{\widehat{I}}{2}[\delta(E-\sqrt{\mu_2}) + \delta(E+\sqrt{\mu_2})], \qquad (6)$$

and the attractive part of the energy of interatomic interaction for $N_\mathrm{d} < 5$ is given by $-N_\mathrm{d}\sqrt{\mu_2}$, where

$$\mu_2 = \frac{3}{10}\sum_{\beta\neq\alpha}[(\mathrm{dd}\sigma)(R_{\alpha\beta})]^2. \qquad (7)$$

In this limit the angular character of matrix elements $(0|\widehat{H}^2|0)$ is neglected and the denominator of (2) has two five-fold degenerate roots. The function $\rho(\ldots)$ of the Finnis–Sinclair model (1) can in this case be identified with $(3/10)N_\mathrm{d}^2(\mathrm{dd}\sigma)^2$. One should note though that the Finnis–Sinclair model (1) in fact goes beyond the naive assumption that the function $\rho(\ldots)$ is *actually* proportional to the square of the tight-binding hopping integral $(\mathrm{dd}\sigma)$. The fact that functions $\rho(\ldots)$ and $V(\ldots)$ in Eq. (1) approximate the behaviour of a real material rather than a model 'second-moment' system means that effectively these two functions include higher-order terms going beyond (6).

The derivation given above illustrates the limitation of the model (1), that does not include the second-moment angular terms given by (A.1). To investigate the part played by these terms we include them as a correction added to the core region of the original potential (1). The function $\rho(\ldots)$ of the model (1) is now replaced by a 5×5 matrix

$$\rho_{ij}(r,\theta,\phi) = \frac{1}{N_d^2}\rho(r)\delta_{ij} + \left[\mathscr{D}^2_{ij}(\theta,\phi) - \frac{3}{10}\delta_{ij}\right]g(r) + \cdots, \qquad (8)$$

where the second 'quantum core' term is chosen to have a functional form somewhat resembling that of the quadrupole term of classical electrostatics. The function $g(r)$ is chosen bearing in mind that the quantum core correction should only be significant at distances smaller than the distance between nearest neighbours in a perfect crystal lattice and that the quantity $\rho_{ij}(r,\theta,\phi)$, as well as its first and second derivatives, should remain continuous everywhere within the interval of variation of parameters r, θ, ϕ encountered in a simulation. In the example described below the function $g(r)$ for bcc vanadium was chosen in the form $g(r) = 2.7\times 10^2(r-r_\mathrm{QC})^3/N_\mathrm{d}^2$ for $r < r_\mathrm{QC}$, where the radius r_QC of the quantum core region equals $r_\mathrm{QC} = 2.58$ Å. By choosing the value of r_QC smaller than the distance between nearest neighbour atoms, we make sure that other properties of the original Finnis–Sinclair potential, for example elastic constants, remain entirely unaffected by the presence of the quantum core. The total energy of interatomic interaction in the model (8) is given by,

$$E_\mathrm{tot} = \sum_\alpha\left[-\sum_{n=1}^{5}\Theta_{n\alpha}\sqrt{H_n^2(\alpha)} + \sum_{n=6}^{10}\Theta_{n\alpha}\sqrt{H_n^2(\alpha)}\right] + \frac{1}{2}\sum_{\alpha\neq\beta}V(R_{\alpha\beta}). \qquad (9)$$

Here $H_n^2(\alpha)$ is the n-th eigenvalue of the matrix $(0|\widehat{H}^2|0)$ for atom α and $\Theta_{n\alpha}$ is the occupation number corresponding to this eigenvalue. Quantities $\Theta_{n\alpha}$ satisfy the sum rule $\sum_n \Theta_{n\alpha} = N_\mathrm{d}$.

To illustrate the difference between the introduction of the quantum core corection to the Finnis–Sinclair model and the re-parameterisation of the model (1), in Fig. 2 we plotted the energy–volume curves calculated using density functional theory, the original Finnis–Sinclair potential for vanadium [8], the re-parameterised

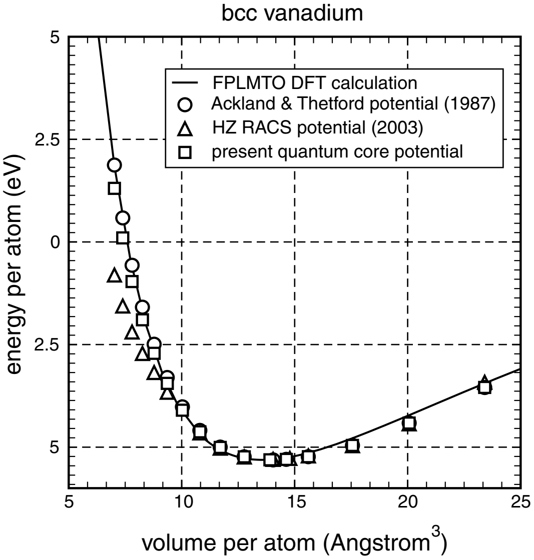

Fig. 2. Energy–volume curves of body-centred cubic vanadium calculated using density functional theory in the local density approximation, the original Finnis–Sinclair potential for vanadium parameterised by Ackland and Thetford [8], the new form of the Finnis–Sinclair potential [1], and the quantum core potential described in the text.

Table 1
Energies of formation of various configurations of single self-interstitial atom defects in body-centred cubic vanadium calculated using density functional theory, two different forms of the Finnis–Sinclair potential, and the quantum core potential described in the text

Orientation	DFT [5]	FS (eV) [8]	FS (eV) [1]	QC ($N_d = 3$) (eV)
111	3.14	4.58	3.27	3.22
110	3.48	4.14	3.66	3.49
100	3.57	4.79	3.60	4.11

Finnis–Sinclair potential for vanadium described in [1], and the quantum core-corrected potential given by Eq. (8) for $N_d = 3$.

Fig. 2 shows a noticeable difference between the energy–volume curve calculated using density functional theory and the re-parameterised Finnis–Sinclair potential given in Ref. [1]. The original form of the Finnis–Sinclair potential [8] as well as the quantum core potential both agree better with the density functional results.

We also carried out preliminary tests of the quantum core potential in simulations of equilibrium configurations of single atom self-interstitial defects. The energies of formation of defects calculated using density functional theory [5] and two versions of the Finnis–Sinclair potentials available in the literature [1,8] are given in Table 1. Values obtained using the quantum core potential agree better with density functional calculations than those found using the original Finnis–Sinclair potential [8]. In comparison with the re-parameterised version of the Finnis–Sinclair potential [1] we find a somewhat more consistent pattern of *ordering* of energies of defects (note that potential [1] predicts the higher formation energy for the 110 self-interstitial configuration in comparison with the 100 configuration). These preliminary results suggest that the approach described in this paper may help in understanding microscopic mechanisms of formation of self-interstitial atom defects in fusion materials.

Acknowledgements

The author acknowledges stimulating discussions with D.G. Pettifor and D. Nguyen-Manh. The author would like to thank P. Derlet for raising the question about the possible significance of the matrix recursion formalism. The author is grateful to I. Cook and J.W. Connor for helpful comments. This work was funded by the UK Engineering and Physical Sciences Research Council and by EURATOM.

Appendix A

The fifteen independent functions describing the angular part of the matrix $(0|\widehat{H}^2|0)_{ij}$ have the form

$$
\begin{aligned}
\mathscr{D}^2_{xy,xy} &= \frac{1}{4}(l^2+m^2+8l^2m^2)\\
\mathscr{D}^2_{xy,yz} &= \frac{1}{4}ln(1+8m^2)\\
\mathscr{D}^2_{xy,xz} &= \frac{1}{4}mn(1+8l^2)\\
\mathscr{D}^2_{xy,x^2-y^2} &= lm(l^2-m^2)\\
\mathscr{D}^2_{xy,3z^2} &= \frac{\sqrt{3}}{2}lm(n^2-l^2-m^2)\\
\mathscr{D}^2_{yz,yz} &= \frac{1}{4}(m^2+n^2+8m^2n^2)\\
\mathscr{D}^2_{yz,zx} &= \frac{1}{4}lm(1+8n^2)\\
\mathscr{D}^2_{yz,x^2-y^2} &= mn\left[l^2-m^2-\frac{1}{4}\right]\\
\mathscr{D}^2_{yz,3z^2} &= \frac{\sqrt{3}}{4}mn[3n^2-(l^2+m^2)]\\
\mathscr{D}^2_{zx,zx} &= \frac{1}{4}(n^2+l^2+8n^2l^2)\\
\mathscr{D}^2_{zx,x^2-y^2} &= nl\left(l^2-m^2+\frac{1}{4}\right)\\
\mathscr{D}^2_{zx,3z^2} &= \frac{\sqrt{3}}{4}ln[3n^2-(l^2+m^2)]\\
\mathscr{D}^2_{x^2-y^2,x^2-y^2} &= \frac{(l^2-m^2)^2}{2}+\frac{(l^2+m^2)}{4}\\
\mathscr{D}^2_{x^2-y^2,3z^2} &= \frac{\sqrt{3}}{4}(l^2-m^2)[n^2-l^2-m^2]\\
\mathscr{D}^2_{3z^2,3z^2} &= \frac{1}{4}[4n^4-n^2(l^2+m^2)+(l^2+m^2)^2],
\end{aligned}
\tag{A.1}
$$

where $l = \sin\theta\cos\phi$, $m = \sin\theta\sin\phi$ and $n = \cos\theta$ are the direction cosines of the direction of the interatomic bond, and θ and ϕ are the azimuthal and polar angles defined in a chosen Cartesian system of coordinates.

References

[1] S. Han, L.A. Zepeda-Ruiz, G.J. Ackland, R. Car, D.J. Srolovitz, J. Appl. Phys. 93 (2003) 3328.

[2] L.A. Zepeda-Ruiz, S. Han, D.J. Srolovitz, R. Car, B.D. Wirth, Phys. Rev. B 67 (2003), art. no. 134114.

[3] F. Willaime, A. Satta, M. Nastar, O. Le Bacq, Int. J. Quantum Chem. 77 (2000) 927.

[4] C. Domain, C.S. Becquart, Phys. Rev. B 65 (2001), art. no. 024103.

[5] S. Han, L.A. Zepeda-Ruiz, G.J. Ackland, R. Car, D.J. Srolovitz, Phys. Rev. B 66 (2002), 220101.
[6] D. Yessilleten, M. Nastar, T.A. Arias, A.T. Paxton, S. Yip, Phys. Rev. Lett. 81 (1998) 2998.
[7] M.W. Finnis, J.E. Sinclair, Philos. Mag. A 50 (1984) 45.
[8] G.J. Ackland, R. Thetford, Philos. Mag. A 56 (1987) 15.
[9] G.J. Ackland, D.J. Bacon, A.F. Calder, T. Harry, Philos. Mag. A 75 (1997) 713.
[10] D.G. Pettifor, in: Proceedings of the Materials Modelling Laboratory Workshop, Oxford, September 1999.
[11] A.E. Carlsson, Phys. Rev. B 44 (1991) 6590.
[12] S.M. Foiles, Phys. Rev. B 48 (1993) 4287.
[13] L.D. Landau, E.M. Lifshits, Quantum Mechanics, Non-relativistic Theory, 3rd Ed., Pergamon, Oxford, 1977, p. 138.
[14] J. Inoue, Y. Ohta, J. Phys. C: Solid State Phys. 20 (1987) 1947.
[15] D.G. Pettifor, I. Oleinik, Phys. Rev. B 59 (1999) 8487.
[16] S.L. Dudarev, Phys. Rev. B 65 (2002), art. no. 224105.
[17] J.C. Slater, G.F. Koster, Phys. Rev. 94 (1954) 1498.