

A NEW PSEUDOPOTENTIAL FOR SIMPLE METALS

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ABSTRACT

We propose a local pseudopotential $w(r)$ for simple metals, which displays an exponential decay of the core repulsion as $r \rightarrow \infty$ and is analytic for all r . The Fourier transform $w(Q)$ is also an analytic function, and decays rapidly as $Q \rightarrow \infty$. Inputs to the pseudopotential are the average electron density \bar{n} at which the bulk metal is stable, the valence z , and the single zero Q_0 of $w(Q)$ or, alternatively, the number of interstitial valence electrons. Binding energies, bulk moduli, and pressure derivatives of the bulk moduli, evaluated in second-order perturbation theory, are in good agreement with experiment.

1. Introduction

Various pseudopotentials are available today, starting from simple semi-empirical models and ending with sophisticated first-principles potentials. Local pseudopotentials are often very convenient.^{1,2}

The inputs to a local pseudopotential should be the most important parameters of simple metals, such as the average electron density, the valence, and the first zero of its Fourier transform. We propose a new local pseudopotential, with these inputs, which is continuous and has continuous derivatives. We were motivated to search for such a smooth local pseudopotential by two main considerations: (1) Smoothness leads to a better convergence of sums over reciprocal lattice vectors. (2) Smoothness and evanescence (exponential decay of the core repulsion as $r \rightarrow \infty$) are properties to be expected from the orthogonalized plane wave construction² of a pseudopotential.

Our "evanescent core" pseudopotential may be written as

$$w(r) = -\frac{z}{R} \left\{ \frac{1}{x} [1 - (1 + \beta x)e^{-\alpha x}] - Ae^{-x} \right\}, \quad (1)$$

with $x = r/R$, R being a core decay length, and with $\alpha > 0$. At $r = 0$, our potential is designed to have a finite value and vanishing first and third derivatives. This condition determines the constants A and β in terms of α and R and leads to a quick convergence of $w(Q)$ when $Q \rightarrow \infty$: $w(Q) \rightarrow Q^{-8}$. At large r , our

potential approaches the Coulomb tail, with a contribution from the core which decays exponentially.

The potential depends only on R when the single zero of its Fourier transform, given by $(Q_0 R)^2 = 2/(\alpha^2 - 3)$, is chosen in order to agree with the position of the zero of the empirical Heine-Abarenkov-Animalu form factor. The condition of bulk stability determines R for a given valence z and density. An alternative is to adjust α to the number of valence electrons in the interstitial region. We have calculated this number using an all-electron, full-potential LASTO or linearized-augmented-Slater-type-orbital³ program.

The pseudopotential has been tested for the simple metals, in the framework of second order perturbation theory and using local-field exchange-correlation corrections to the Lindhard dielectric function. We have evaluated binding energies e , bulk moduli B , and pressure derivatives of bulk moduli $B' = dB/dP$, at equilibrium densities of various metals, and compared them with experimental values.

2. Results

The binding energy per electron is

$$e = e^J + e_M + \bar{w}_R + \epsilon_{bs} \quad , \quad (2)$$

with e^J the binding energy of the jellium model, $e_M = -9z^{2/3}/(10r_s)$ the Madelung energy, $\bar{w}_R = 4\pi\bar{n}R^2 \left[\frac{1}{\alpha^2} + 2 \left(\frac{\beta}{\alpha^3} + A \right) \right]$ the average repulsive part of the pseudopotential, and ϵ_{bs} the band-structure energy

$$\epsilon_{bs} = \frac{1}{2} \sum_{\mathbf{G} \neq 0} \left(\frac{\bar{n}_i}{\bar{n}} \right)^2 |w(\mathbf{G})|^2 \frac{\chi(\mathbf{G})}{\epsilon(\mathbf{G})} \bar{n} \quad , \quad (3)$$

where \mathbf{G} denotes a reciprocal lattice vector, \bar{n}_i denotes the average ion density, $\chi(\mathbf{G}) = -\frac{k_F}{\pi^2} \left[\frac{1}{2} + \frac{1-y^2}{4y} \log \frac{1+y}{1-y} \right]$ with $y = \frac{G}{2k_F}$, and $\epsilon(\mathbf{G}) = 1 - 4\pi \frac{\chi(\mathbf{G})}{G^2} [1 - \mathcal{G}_{xc}(\mathbf{G})]$, with $\mathcal{G}_{xc}(\mathbf{G}) = \left[1 - \frac{k_F^2}{\pi} \frac{\partial^2}{\partial \bar{n}^2} (\bar{n} \epsilon_c) \right] y^2$, is the Lindhard dielectric function. The individual values of α were taken from Ref. 2 in the case of fitting the zero of the form factor (choice A) and from the number of interstitial electrons, which, to first order in $w(\mathbf{G})$, reads as

$$N_{int} = z \frac{\Omega_0 - \Omega_{min}}{\Omega_0} - \sum_{\mathbf{G} \neq 0} \frac{4\pi w(\mathbf{G}) \chi(\mathbf{G})}{\Omega_0 G^3 \epsilon(\mathbf{G})} [\sin x - x \cos x]_{|x=G r_{min}} \quad , \quad (4)$$

with Ω_0 the volume of the Wigner-Seitz sphere and $\Omega_{min} = \frac{4}{3}\pi r_{min}^3$ the volume of the "touching" or "inscribed" sphere (choice B). The equilibrium condition is

$$\frac{\partial}{\partial r_s} e(r_s, z, R) = 0 \quad . \quad (5)$$

Metal	r_s	z	struc.	$Q_0/2k_F$	N_{int}	α	R	R_{HF}
<i>Al</i>	2.07	3	fcc	A	0.74	0.744	3.596	0.327
				B	0.76	0.717	3.570	0.321
<i>Mg</i>	2.65	2	hcp $c/a=1.625$	A	0.79	0.554	3.611	0.390
				B	0.76	0.577	3.660	0.396
<i>Na</i>	3.93	1	bcc	A	0.89	0.399	3.800	0.481
				B	0.99	0.350	3.390	0.502

Table 1. Parameters of the evanescent core potential using choice A and B. The parameters α and R are determined from r_s , z and Q_0 for a given lattice structure, in choice A, and from r_s , z and N_{int} for a given lattice, in choice B. For *Mg*, in choice B, we have used the "nominal" fcc structure instead of the real hcp structure. R_{HF} is the Hartree-Fock decay length of the highest s or p core orbital. The unit of r_s , R and R_{HF} is the *bohr*.

Metal		$-e$	B	B'
<i>Al</i>	SJ	19.10	1.576	3.2
	A	18.82	0.864	4.5
	B	19.03	0.805	4.4
	X	18.88	0.794	4.7
<i>Mg</i>	SJ	12.39	0.487	3.2
	A	11.97	0.351	4.2
	B	11.89	0.379	4.2
	X	12.10	0.369	3.9
<i>Na</i>	SJ	6.34	0.076	3.2
	A	6.20	0.075	3.7
	B	6.26	0.071	3.6
	X	6.25	0.073	3.9

Table 2. Bulk binding energy per electron e , bulk modulus B , and pressure derivative of the bulk modulus B' for the choices A and B of the evanescent core potential. SJ labels the stabilized jellium result, while X refers to experimental values. The unit of the binding energy is the eV , while the unit of B is the $Mbar$ ($1 \text{ hartree} = 27.21 \text{ eV}$, $1 \text{ hartree}/\text{bohr}^3 = 294.2 \text{ Mbar}$).

Table 1 shows the values of R for Al, Mg and Na. Comparing R with the Hartree-Fock decay length $R_{HF} = 1/\sqrt{-2\epsilon_{HF}}$, with ϵ_{HF} the Hartree-Fock energy of the highest core orbital of s or p type,⁴ we note the good agreement. This fact corroborates the physical picture upon which the pseudopotential has been built.

The bulk modulus is

$$B = -V \left(\frac{\partial P}{\partial V} \right)_N = \frac{1}{12\pi} \left(\frac{1}{r_s} \frac{\partial^2 e}{\partial r_s^2} - \frac{2}{r_s^2} \frac{\partial e}{\partial r_s} \right) \quad (6)$$

with $P = - \left(\frac{\partial E}{\partial V} \right)_N$ the pressure. The pressure derivative of the bulk modulus is $B' = \frac{dB}{dP}$.

Table 2 shows the output of our calculations of equilibrium binding energies, bulk moduli, and pressure derivatives of the bulk moduli for Al, Mg and Na. For the sake of comparison, we display also the values obtained with the stabilized jellium model,⁵ which does not consider band-structure effects. The new results are better than those of stabilized jellium. Comparison of Tables 1 and 2 shows that an increase in the interstitial electron number enhances the bulk modulus or elastic stiffness, as expected.

3. Conclusions

We have proposed a local pseudopotential $w(r)$ with an exponentially decaying repulsion from the core at large r and simple analyticity conditions at small r . A second-order perturbative calculation with these pseudopotentials has shown good agreement of the predicted physical properties with experiment.

References

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