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Equation of state for transition metals

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A mixed power-exponential-type potential is proposed for transition metals that overcomes two of the key problems associated with the extended Rydberg potential formalism of the Rose binding-energy relation and the Vinet equation of state. First, it includes naturally the hard-core repulsion at high pressures, and secondly it avoids the convergency problems associated with the series expansion of the Rydberg potential about equilibrium. This potential has been tested against an extensive first-principles database across the transition-metal series. It should prove invaluable to experimentalists in the fitting of their high-pressure data and to theorists in the development of robust interatomic potentials for atomistic simulations.

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Both the analysis of experimental high-pressure data and the validity of theoretical atomistic simulations rely on models of the volume dependence of the energy. For example, shortcomings in the parametrization of the binding-energy relation (or energy versus volume curve) at high pressure render the molecular-dynamics simulations of collision cascades in radiation damage unreliable.[1] Similar problems would arise with the corresponding equation of state (or pressure versus volume curve). While today routine first-principles simulations may be used to gauge the robustness of the binding-energy relations or equations of state, physically based analytic representations are still lacking. In this Rapid Communication, therefore, we analyze two popular descriptions, based on the Rydberg potential,[2] namely the Rose binding-energy relation[3] and the Vinet equation of state,[4] and contrast these with the more physically motivated generalized Morse potential[5] for the case of elemental transition metals. This will allow us to pinpoint the failures of this wide class of equations of state, thereby leading to an improved analytic representation.

The Rose binding-energy relation and the Vinet equation of state were published about 20 years ago and made claims of universality across a broad range of materials.[3,4] The expressions of Rose and Vinet turned out to be two different variants of the extended Rydberg potential,[6] namely

$$E^*_{\mathrm{er}}(x^*) = E_{\mathrm{er}}/E_0 = -\left(1 + x^* + \sum_{n=2} c^{(n)}(x^*)^n\right)e^{-x^*}, \tag{1}$$

where the explicit series expansion extended the original Rydberg potential.[2] E^*_{er} is the binding energy scaled by the cohesive energy at equilibrium E_0, whereas $x^* = (V^{1/3} - V_0^{1/3})/l$ is a scaled distance measuring the difference in the cube root of the volume per atom $V^{1/3}$ from its equilibrium value $V_0^{1/3}$.

Rose *et al.*[3] fixed the scaling length $l = l_r$ of their *binding-energy relation* by constraining Eq. (1) to satisfy the boundary conditions $E^*(0) = -1$, $E^{*\prime}(0) = 0$, and $E^{*\prime\prime}(0) = 1$, fitting the values of E_0, V_0, and K_0, where K_0 is the equilibrium bulk modulus. The resultant Rose scaling length is found to be

$$l_r = V_0^{1/3}/\sqrt{9V_0K_0/E_0}, \tag{2}$$

which is of a similar form to that given in the 1931 Rydberg paper.[2] Rose *et al.* included up to the cubic term in Eq. (1), assuming the coefficient $c_r^{(3)}$ to be independent of materials so that their binding-energy relation remained "universal."

Vinet *et al.*,[4] on the other hand, fixed their scaling length l_v by constraining Eq. (1) to satisfy the three boundary conditions that are appropriate for an *equation of state*, namely V_0, K_0, and K_0', where K_0' is the pressure dependence of the bulk modulus at equilibrium. This led to an equation of state of the form

$$H_v = P_v x^2/[3(1-x)] = K_0 e^{-(x-1)(V_0^{1/3}/l_v)} = K_0 e^{-x_v^*}, \tag{3}$$

where $x = (V/V_0)^{1/3}$ and the Vinet scaling length is given by

$$l_v = V_0^{1/3}/[3(K_0' - 1)/2]. \tag{4}$$

In fact, this so-called Vinet equation of state had already been written down five years earlier by Stacey,[7] who had also started from the Rydberg form for the potential.[6] Equation (3) gave a novel way for analyzing experimental pressure data since plotting the logarithm of H_v against the Vinet length x_v^* should result in a universal linear dependence with the line having a slope of −1.

Unfortunately, numerous authors[8–11] have pointed out that most materials deviate from these so-called universal binding-energy and pressure relationships. Not only is the analytic coefficient $c_r^{(3)}$ in the Rose universal binding-energy relation very material-dependent through K_0',[12] but higher-order derivatives K_0'', K_0''', $K_0^{IV}, \ldots$ can make significant contributions to the Vinet equation of state above about 100 GPa.[13] Although these can be included in principle through the higher-order terms in extended Rydberg or ln H series expansions,[8–10] the higher-order coefficients are found to oscillate with increasing amplitude[13] reminiscent of a divergent series.[14]

In this Rapid Communication, we address these problems of the extended Rydberg potential and corresponding equation of state by discussing first the more physically motivated generalized Morse potential[5,15,16] and then suggesting an improved analytic form that overcomes some of the inherent difficulties with analytic potentials. It is widely accepted that covalently bonded materials, whether *sp*-valent systems[15] with saturated bonds or *d*-valent transition metals with unsaturated bonds,[16,17] can be described by a generalized Morse potential with exponential form

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$$E_{\mathrm{gm}}(x) = Ae^{-p(x-1)} - Be^{-q(x-1)}, \tag{5}$$

where the first contribution arises from the overlap repulsion, and the second from the formation of covalent bonds.[18] Assuming that the overlap repulsion falls off with distance as the square of the bond integral,[19] Eq. (5) takes the simple Morse form[5] corresponding to $p = 2q$.

Whereas the original Rydberg and Morse potentials contain three fitting parameters, the generalized Morse potential contains four parameters A, B, p, and q. They can be obtained by fitting the three equilibrium properties V_0, K_0, and K_0' with the fourth input being either E_0 for the binding-energy relation or K_0'' for the equation of state. We find that the *arithmetic mean* of the exponents p and q is given by

$$(p+q)/2 = 3(K_0' - 1)/2 = V_0^{1/3}/l_v, \tag{6}$$

whereas the *geometric mean* is dependent on whether E_0 or K_0'' is fitted, namely

$$\sqrt{pq} = \begin{cases} \sqrt{7 - 9(K_0K_0'' + K_0')} & \text{for } K_0'', \\ \sqrt{9V_0K_0/E_0} = V_0^{1/3}/l_r & \text{for } E_0. \end{cases} \tag{7}$$

The latter expression for the Rose length had been determined earlier by Spanjaard and Desjonquères[20] in their analysis of the link between the second-moment tight-binding model and the Rose binding-energy relation.[3] However, in practice the arithmetic mean is the natural inverse scaling length for the generalized Morse potential with its sum of two exponentials, as Eq. (5) can be rewritten as

$$E^*_{\mathrm{gm}}(x^*_v) = -[\sinh(\sqrt{\mu}x^*_v)/\sqrt{\mu} + \cosh(\sqrt{\mu}x^*_v)]e^{-x^*_v}, \tag{8}$$

where

$$\mu = [(p-q)/(p+q)]^2 = 1 - [2\sqrt{pq}/(p+q)]^2. \tag{9}$$

Let us first consider the case of the four-parameter generalized Morse *binding-energy relation* where the cohesive energy E_0 is used as an input fitting parameter. Then substituting Eq. (6) and the lower Eq. (7) into Eq. (9), we have $\mu = 1 - (l_v/l_r)^2$. Thus, μ will be positive or negative depending on whether l_v is less than or greater than l_r. This reflects the behavior of the cubic prefactor $c_r^{(3)}$ in the Rose binding-energy relation since $c_r^{(3)} = (1/\sqrt{1-\mu} - 1)/3$, which can be obtained directly by expanding Eq. (8) in the Rose form. The left-hand panel of Fig. 1 shows the variations of μ and $c_r^{(3)}$ across the 4d transition-metal series that is predicted by density-functional theory (DFT). We have used the VASP package[21] with projected augmented wave (PAW) pseudopotentials[22] within the local-density approximation (LDA).[23] In order to obtain accurate data at high pressures, the semicore electrons are treated as valence electrons.[24] A large cutoff energy of 430 eV is taken, and the **k**-point mesh is chosen as $(45/2\pi)$ times the length of the reciprocal vector (e.g., $15 \times 15 \times 9$ is used for hcp Y at equilibrium). Binding-energy curves are calculated for all three common metallic structure types bcc, fcc, and hcp (with c/a fixed as the equilibrium value).

We see immediately that neither the generalized Morse parameter μ nor the Rose parameter $c_r^{(3)}$ is a universal parameter, since they range from negative to positive across the series for all three structure types. Although this confirms that the Rose universal binding-energy relation is very far from universal, it also highlights a severe deficiency of the generalized Morse potential when applied to the early transition metals, since negative values of μ imply that $\sqrt{\mu}$ in Eq. (8) is imaginary. Thus we have lost the physical basis of the generalized Morse potential because p and q will be complex and we can no longer separate out the terms in Eq. (8) into real repulsive and attractive contributions as in Eq. (5). This imaginary behavior of $\sqrt{\mu}$ leads to the hyperbolic functions in Eq. (8) being replaced by their trigonometric counterparts,[25] so that the generalized Morse binding-energy curves for the early transition metals would oscillate at large volume expansions.

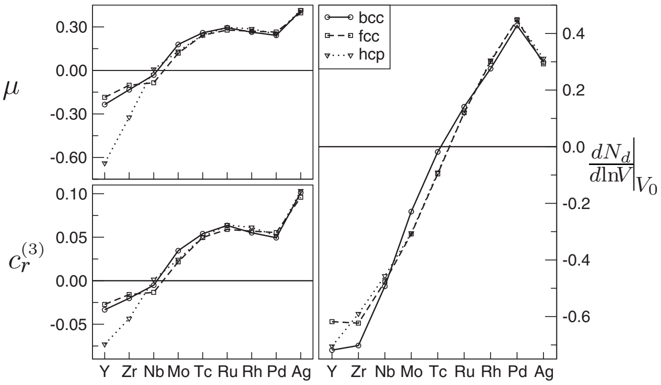

FIG. 1. Trend of Morse parameter μ, Rose parameter $c_r^{(3)}$, and logarithmic volume derivative of number of valence d electrons at equilibrium across 4d transition-metal series.

The origin of this spurious oscillatory behavior appears to be related to the $s \rightarrow d$ electron transfer under pressure, as the logarithmic volume derivative of the number of valence d electrons in the right-hand panel of Fig. 1 displays a similar trend to that of μ and $c_r^{(3)}$ in the left-hand panel[28]. Therefore, for early transition metals, the four-parameter generalized Morse potential (4-gm) with real values of p and q is unable to reproduce simultaneously the values of V_0, K_0, and K_0' *at equilibrium* and E_0, which depends on the total area under the equation of state as the atoms are brought together *from infinity*.

Let us now consider the case of the four-parameter generalized Morse (4-gm) *equation of state* where K_0'' rather than E_0 is used as an input fitting parameter. It follows from Eq. (8) that the equation of state takes the compact form

$$H^*_{\mathrm{gm}} = \frac{P_{\mathrm{gm}}x^2}{3K_0(1-x)} = \frac{\sinh(\sqrt{\mu}x^*_v)}{\sqrt{\mu}x^*_v}e^{-x^*_v}, \tag{10}$$

where $H^* = H/K_0$ and μ is given by Eq. (9) using Eq. (6) and the upper Eq. (7). We see immediately that we recover the Vinet equation of state, Eq. (3), in the limit as $\mu \rightarrow 0$, corresponding to $p \rightarrow q$.

Figure 2 compares the 4-gm binding-energy relation, equation of state, and ln H^* plots with the DFT curve for hcp Y. The inset in the lowest panel shows that the predicted value of the cohesive energy, namely E_0(4-gm) = 10.98 eV

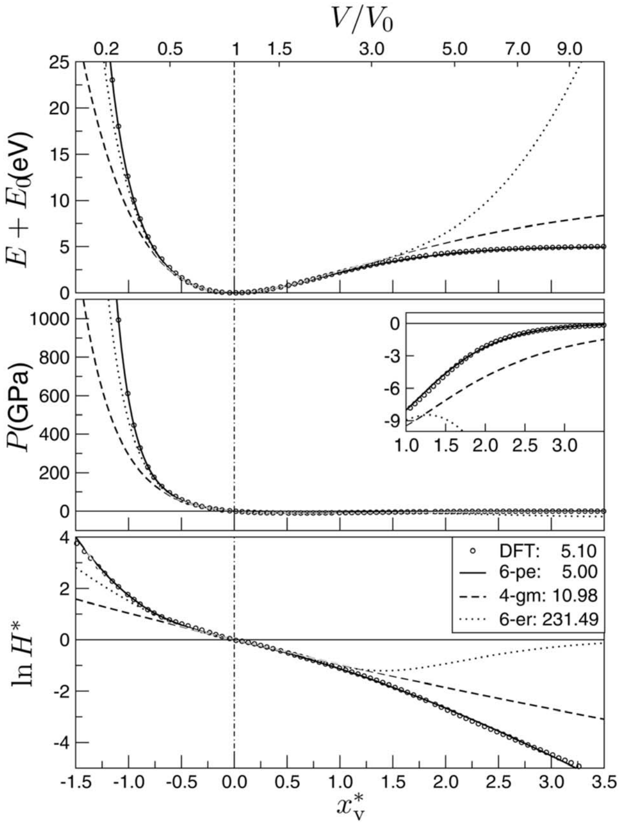

FIG. 2. Shifted binding energy, pressure, and normalized $\ln H^*$ plots for hcp Y. Open circles: DFT reference data; solid line: six-parameter power-exponential potential (6-pe); dashed line: four-parameter generalized Morse potential (4-gm); dotted line: six-parameter extended Rydberg potential (6-er). The predicted cohesive energies E_0, which are obtained by integrating analytically the different equations of state, are given (in eV) in the inset of the lowest panel.

(obtained by integrating analytically the pressure-volume curve from equilibrium out to infinity), is in poor agreement with the DFT value of 5.10 eV. This reflects the sizeable 4-gm deviations from the equation of state and $\ln H^*$ DFT curves in Fig. 2 as the atoms are pulled apart to infinity, and is responsible for the spurious oscillatory behavior found earlier in the binding-energy relation when the cohesive energy was constrained to take the DFT values. In addition, we see that under compression for pressures greater than about 100 GPa there are sizeable differences between the 4-gm and DFT curves due to the neglect of the hard-core repulsion in this exponential-type potential. As stressed by Stacey[26] and Holzapfel,[14] both the Rydberg and Morse potentials have $K'_\infty = \frac{2}{3}$ at infinite pressure, whereas it is known experimentally that the iron core of the Earth, for example, takes the infinite pressure asymptote of $K'_\infty = 3.0 \pm 0.1$.[25] Clearly the expected divergence of the interatomic potential at high pressures is not displayed by exponential functions.

We have, therefore, attempted to rectify these problems within the 4-gm potential by fitting a six-parameter potential with a mixed power-exponential (6-pe) form, namely

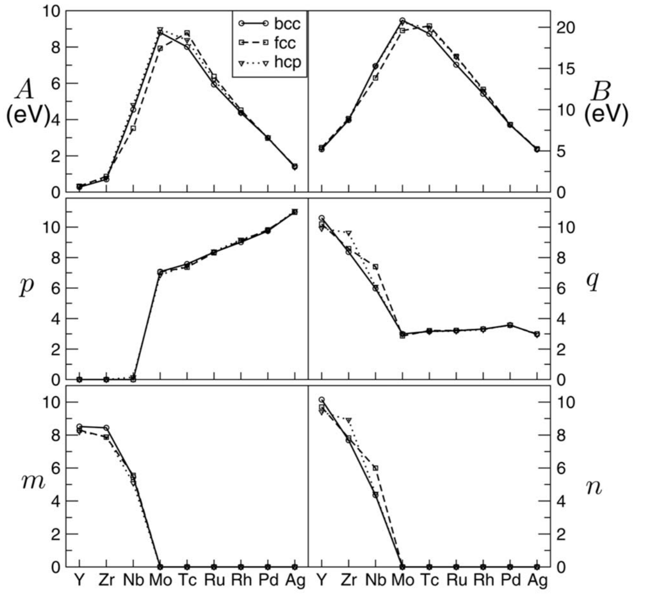

FIG. 3. Trend of 6-pe parameters across 4d transition-metal series.

$$E_{\rm pe} = A\frac{e^{-p(x-1)}}{x^m} - Bx^n e^{-q(x-1)}, \qquad (11)$$

with $m, n \geqslant 0$. The first contribution takes care of the divergence in the repulsive energy as $x \to 0$, whereas the second attractive contribution has an additional degree of freedom for fitting the binding-energy curve as the atoms are pulled apart to infinity. This potential leads to the six-parameter equation of state

$$H^*_{\rm pe} = \frac{(p+m/x)(q-n)x^{-m}e^{-p(x-1)} - (p+m)(q-n/x)x^n e^{-q(x-1)}}{\{(p+m)(q-n)[(p+m)-(q-n)]+(pn+qm)\}(1-x)},$$

where $x = (V/V_0)^{1/3}$ and $H^* = Px^2/[3K_0(1-x)]$ are determined by inputting the values of the equilibrium volume V_0 and K_0, respectively. The remaining four parameters p, q, m, and n will be determined in this Rapid Communication by fitting the equation of state from 1000 GPa to $7V_0$.

We see from Fig. 2 that the comparisons between this analytic 6-pe potential and DFT are excellent, with the 6-pe curves passing straight through all the DFT points. This is reflected by the good agreement between the predicted value of the cohesive energy, namely E_0 (6-pe) = 5.00 eV, and the DFT value of 5.10 eV. We have performed similar calculations across the 3d, 4d, and 5d transition-metal series, finding corresponding levels of agreement for the binding-energy curves and equations of state to those displayed in Fig. 2 for Y.[27] The one exception is Sc, where the $\ln H^*$ plot first shows a small softening under pressure before the hard-core contribution kicks in. This requires extending the present 6-pe potential to include a further two parameters and will be discussed elsewhere.[27]

Figure 3 shows the predicted variation of the six parameters A, B, p, q, m, and n across the 4d series. We see that both A and B reflect the well-known parabolic behavior of the cohesive energy across the transition-metal series as first the bonding and then the antibonding d states are filled with valence electrons.[18] This is not unexpected given that at equilibrium $E_0=B-A$ from Eq. (11). Interestingly, we also observe that for pressures less than 1000 GPa, the repulsive part of the potential is either a pure power law ($p=0$, $m \neq 0$) for the early transition metals or a pure exponential law ($p \neq 0$, $m=0$) for the middle and late transition metals. The attractive part of the potential, on the other hand, is either pure exponential ($q \neq 0$, $n=0$) for the middle and late transition metals or of mixed power-exponential form ($q \neq 0$, $n \neq 0$) for the early transition metals. Thus, for P less than 1000 GPa, the middle and late transition metals are well described by the 4-gm potential, with the hard-core contribution only becoming noticeable at much higher pressures.[27]

We can also compare the predictions of the six-parameter extended Rydberg potential (6-er) against the DFT and 6-pe potential in Fig. 2. Retaining contributions up to $n=5$ in Eq. (1), the resultant six independent parameters in the equation of state can be determined from the 6-pe values for V_0, K_0, and the analytic derivatives K_0', K_0'', K_0''', and K_0^{IV} that are implicit in the six potential parameters in Fig. 3. We see that the dotted curves in Fig. 2 that represent this 6-er potential fail to reproduce both the hard-core contribution to the ln H^* plot at high pressures and the behavior of the binding-energy curve at large volumes. This failure results in a predicted value of the cohesive energy that is 40 times larger than that of DFT. Thus, a Taylor expansion about equilibrium is not a mathematically sensible way to proceed if one also wishes to reproduce the binding-energy curve at large volumes or the equation of state at high pressures.

In conclusion, we have proposed an analytic potential for transition metals that overcomes two of the key problems with the extended Rydberg formalism of the Rose binding-energy relation and the Vinet equation of state. First, by having a mixed power-exponential form, it naturally includes the hard-core repulsion that is observed in the early transition metals under high pressure. Secondly, by comprising physically motivated repulsive and attractive contributions, it avoids the convergency problems at either high pressures or large volumes that are associated with the series expansion of the Rydberg potential about equilibrium. This mixed power-exponential-type potential has been tested against an extensive DFT database across the transition-metal series. It should prove invaluable to experimentalists in the fitting of high-pressure data and to theorists in the development of robust interatomic potentials for atomistic simulations.

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