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Impurity potentials derived from embedded quantum clusters: Ag^+ and Cu^+ transport in alkali halides

Jie Meng[†], Ravindra Pandey[†], John M Vail[‡] and A Barry Kunz[†]

[†] Department of Physics, Michigan Technological University, Houghton, Michigan 49931, USA

[‡] Department of Physics, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

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Abstract. Short-range shell-model potentials between substitutional Ag^+ ions and host-lattice halide ions in RbCl, KCl, NaCl, and NaF are derived using the ICECAP methodology. In this method the impurity and its nearest neighbours are treated as an embedded quantum cluster in unrestricted Hartree–Fock self-consistent field approximation. The embedding lattice is described by the shell model. The consistency of the derivation is tested in various ways. The potentials are then applied to calculate activation energies for diffusion by vacancy and interstitial mechanisms for Ag^+ . Previously derived potentials for Cu^+ are used to calculate interstitial diffusion activation energies in KCl and NaCl. The potentials are tested for transferability from one host crystal to another. Deficiencies of the method are discussed and improvements are identified.

1. Introduction

In an earlier work (Meng *et al* 1988) we derived shell-model short-range potentials for Cu^+ in some alkali halides, and applied them to diffusion by the vacancy mechanism with apparently reasonable results. The objectives of the present work are to extend the procedure to Ag^+ impurities, to include diffusion by the interstitial mechanism, and to test some assumptions of the previous work.

Certain assumptions are commonly made in applying the shell model to defects in ionic crystals. One such assumption is that, although the model has been derived from macroscopic properties that involve only small deviations from equilibrium, it may be applied to defect configurations that deviate strongly from equilibrium. This assumption is supported by a considerable body of evidence, one of the major works being that of Catlow *et al* (1979a), in which self-diffusion in the alkali halides was studied. It is well known that, from a given set of macroscopic data, one can often derive different shell-model potentials which, although they fit the input data equally well, give significantly different results when applied to defect processes. In this work, the point is illustrated explicitly for impurity potentials which cannot be derived from macroscopic properties, but which instead require quantum-mechanical derivation. Another common assumption is that the shell-model potential between a pair of ions, derived for one particular crystal, may be transferred to another crystal with a different chemical and/or crystallographic composition. An important work where this assumption has been justified

is the work of Catlow *et al* (1978), who successfully simulated the off-centre configuration of small impurities in the alkali halides. In the present work we give a quantitative assessment of the transferability of potentials for Ag^+ in alkali chlorides, and we find discrepancies ≥ 0.1 eV in the calculated activation energies for diffusion by the collinear vacancy mechanism.

An earlier work in which shell-model potentials for Ag^+ have been derived is that of Catlow *et al* (1979b), who analysed $\text{AgCl}:\text{Na}^+$, as well as pure AgCl . We have incorporated their potentials in some of our calculations, as part of the test of transferability. The only experimental data that we know of for Ag^+ diffusion in alkali halides is the deduction by Pershitz *et al* (1981), of interstitial activation energies in NaCl and in KCl . We shall refer to these results later. The Ag^+ ion has properties that are not adequately simulated by the simple shell-model. Jacobs *et al* (1980), have introduced quadrupole deformability of Ag^+ into the shell model, with good results. Bilz (1985) has emphasised the importance of such a feature when discussing the properties of Ag^+ in general. We will comment on this in the quantum-mechanical context at the end of the paper.

In § 2, we briefly describe our method of deriving shell-model impurity potentials, and the physical model on which the calculations are based, including input data. In § 3, we present and discuss our results, including the derived potentials, calculated activation energies for Ag^+ diffusion by vacancy and interstitial mechanisms, with details of the configurations involved. In § 4, we state our conclusions and point out the direction that future analysis of such systems might follow.

2. Method and model

Our method (Meng *et al* 1988), briefly stated, is to simulate the substitutional impurity and its near neighbours in the lattice quantum-mechanically, while the rest of the embedding lattice is represented by the shell-model. The quantum-mechanical region is then expanded and/or compressed by amounts which deviate from equilibrium by several percent (typically about 6%). The resultant dependence of total defect lattice energy on distortion is then compared with that obtained from a set of calculations in which all ions, including the impurity and its near neighbours, are represented by the shell-model. The form of the short-range impurity potential is then chosen so as to produce agreement between the energy variations obtained from the two sets of calculations.

In the present work, the quantum-mechanical region, referred to as an embedded quantum cluster, contains the substitutional impurity Ag^+ ion and its six nearest halide-ion neighbours. It is analysed in the unrestricted Hartree–Fock self-consistent field approximation. The basis sets used are taken from the work of Huzinaga *et al* (1984): specifically, for Ag^+ the free Ag^0 contraction set (4333/433/43); for Cl^- the set (433/43); and for F^- the set (43/4). For the shell-model, the short-range potentials are all of the Buckingham form:

$$V(r) = A \exp(-r/\rho) - C/r^6 \quad (1)$$

where r is the shell–shell distance between a pair of ions. We derive the constants (A , ρ , C) for the nearest-neighbour Ag^+ –halide interaction, assuming that all other interactions are known. Since the absolute energies calculated with the quantum cluster and with its shell-model representation differ by an amount that cannot be determined,

a renormalisation constant α must be evaluated such that it can bring the two energy curves into coincidence for appropriate values of (A, ρ, C) . We therefore require (at least) four equations for the four unknown parameters (A, ρ, C, α) . These equations are obtained from four different expanded and/or compressed configurations of the nearest-neighbour clusters (quantum and shell-model), centred on the impurity Ag⁺. For each configuration, $j = 1, 2, 3, 4$, we then have the equation:

$$f_j(A, \rho, C, \alpha) = 0. \quad (2)$$

This system of equations is solved by a library routine (IMSL/ZXSSQ), whose convergence criterion is $\sum_j |f_j|^2 \leq S$. We have taken $S = 10^{-2}$ eV. In all cases we have used the same initial values, $A = 3275$ eV, $\rho = 0.3$ Å, $C = 0.0$ eV Å⁶, $\alpha = -15.0$ eV, except when testing for the consistency of results for different sets of initial values (§ 3, tables 5 and 6).

The coefficient C in the Buckingham potential of equation (1) refers to effects that arise from electronic correlation. In the present work, correlation is neglected. Accordingly we used the initial value of $C = 0$ for the fitting process. The non-zero final values shown in table 2 should be understood simply as representing a parametrisation of the potential, not a measure of the correlation effect. It remains to be seen how a correlation correction applied to our Hartree-Fock method would affect the results presented here. As we mentioned in § 1, quadrupolar deformation of Ag⁺ has been found to be essential for describing its vacancy diffusion process in AgCl. The method of this paper could be extended to take this into account. Recently, it has been shown that anion self-diffusion in AgCl requires three-body potentials (Corish *et al* 1988). The absence of these two features from the present work means that the calculated activation energies for diffusion by the vacancy mechanism cannot be expected to be reliable.

We note that the method described above can be generalised to include derivation of second-neighbour potentials (Ag⁺-host alkali, in the present case), and that this has already been done for the substitutional H⁻ ion in MgO (Pandey and Vail 1989).

The present calculations were done using the ICECAP program (Harding *et al* 1985) for the embedded quantum cluster calculations, and the HADES program (Norgett 1974) for the shell-model-only calculations. ICECAP in fact incorporates HADES, so the treatment of the shell-model is identical in the two cases, namely fully consistent lattice relaxation is provided for ICECAP. ICECAP is an automated, user-friendly program that incorporates several options that were not used in this work, but which we will mention because they could be useful in subsequent work. They include pseudopotential cores for the ions (Bachelet *et al* 1982, Topiol *et al* 1976), Kunz-Klein localising potentials for improved boundary conditions (Kunz and Klein 1978, Kunz and Vail 1988), and Rayleigh-Schrödinger many-body perturbation theory correlation correction (Goalwin and Kunz 1986, Kunz *et al* 1988). The HADES program minimises the total energy of the defect lattice with respect to explicit variation of ionic positions within a finite radius of the defect origin, and in harmonic approximation accurately couples this region with an infinite discrete-ion embedding lattice whose configuration is consistent with the response of the continuum model. HADES allows specific ions (cores and/or shells) to be held fixed, and exempted from the total-energy minimisation. ICECAP consistently embeds a quantum cluster in the HADES calculation.

We now specify the shell model used in this work. The coefficients (A, ρ, C) in equation (1), for host-lattice short-range potentials (anion-anion, cation-cation, and anion-cation) were taken from Catlow *et al* (1977), (set I), who derived unique cation-cation and anion-anion potentials for each ionic species, valid for most rocksalt alkali

Table 1. Ag⁺-host cation shell-model short-range potentials derived by averaging, equations (3a)–(3c).

Host cation	A (eV)	ρ (Å)	C (eV Å ⁶)
Rb ⁺	10607.746	0.2526	212.294
K ⁺	7921.816	0.2481	167.265
Na ⁺	11423.448	0.1986	80.680

halides. These potentials give equilibrium lattice spacings that differ somewhat from the experimental values, but we have done our calculations using the latter, with values taken from Ashcroft and Mermin (1976). The effect of this discrepancy will be discussed for a particular case in the next section, where it is found to be small.

For Cu⁺ impurities (Meng *et al* 1988) we argued that second-neighbour interactions and ionic polarisability might be negligible (Provet *et al* 1977), but this is not likely the case for Ag⁺. Accordingly we have included Ag⁺-host cation interaction derived by an averaging process (Harker, private communication), since suitable compounds of Ag⁺ and K⁺, for example, do not exist from which to transfer such potentials, and we chose not to derive them quantum-mechanically. In the averaging process, if M is Ag⁺ and N is the host cation, then

$$1/\rho_{MN} = \frac{1}{2}(1/\rho_{MM} + 1/\rho_{NN}) \quad (3a)$$

$$A_{MN} = (A_{MM}A_{NN})^{1/2} \quad (3b)$$

$$C_{MN} = (C_{MM}C_{NN})^{1/2}. \quad (3c)$$

In equations (3a–3c), parameters for MM (Ag⁺–Ag⁺) are taken from the AgCl study of Catlow *et al* (1979b), and parameters for NN from Catlow *et al* (1977), for the appropriate host cation in the chloride (set I). The results are given in table 1.

In the HADES calculations, Ag⁺ is represented as having a shell and a core, unlike the rigid Cu⁺ ion of Meng *et al* (1988). The shell charge Y and shell-core force constant K were taken from Catlow *et al* (1979b), namely $Y = -9.4826|e|$, and $K = 597.69 \text{ eV Å}^{-2}$. One can think of deriving the shell parameters of such an impurity, and the present authors (Vail *et al* 1988) have in fact done this for H⁺ in MgO with encouraging results.

HADES and ICECAP use the static lattice approximation, in which finite temperature effects are ignored. This should be borne in mind when assessing the comparison between calculated and experimental activation energies, since the latter were deduced (Pershits *et al* 1981) in the region 600–700 °C.

3. Results

In table 2, we give the parameters (A , ρ , C) of equation (1), as derived by the method of § 2, for the Ag⁺-host anion interaction in RbCl, KCl, NaCl, and NaF, and for comparison with the first three we include Ag⁺-Cl[−] parameters as derived by Catlow *et al* (1979b) for AgCl. Overall, the AgCl parameters are closest to our derived values for NaCl: Ag⁺, which is probably understandable given the nearly equal lattice spacings of AgCl and NaCl (2.77 Å and 2.82 Å) respectively. In table 3 we give the total energies

Table 2. Ag⁺-host anion shell-model short range potentials in alkali halides derived from quantum clusters, equations (1) and (2), and in AgCl from Catlow *et al* (1979b).

	A (eV)	ρ (Å)	C (eV Å ⁶)
RbCl: Ag ⁻	15471.07	0.26293	186.145
KCl: Ag ⁺	11288.45	0.26625	137.601
NaCl: Ag ⁻	4131.36	0.33967	565.455
NaF: Ag ⁺	2678.24	0.26864	0.68042
AgCl	2518.8	0.3272	219.52

Table 3. Total energies E (eV) as functions of Ag⁺-host anion separation d (units: nearest-neighbour lattice spacing, a) for embedded nearest-neighbour clusters.

d (a)	NaF: Ag ⁺	NaCl: Ag ⁺	KCl: Ag ⁺	RbCl: Ag ⁺
0.94	-160120.55	-219356.50	-219038.35	-218916.16
0.98	1.76	6.98	8.21	5.91
1.02	2.35	7.07	7.91	5.55
1.06	2.47	6.84	7.48	5.10

Table 4. Nearest-neighbour equilibrium distances for substitutional on-centre Ag⁺ ions as calculated from ICECAP, and from HADES using the potentials of table 2. Units: nearest-neighbour perfect lattice spacing, a .

	a (Å)	ICECAP	HADES
RbCl: Ag ⁺	3.29	0.900	0.893
KCl: Ag ⁺	3.145	0.934	0.929
NaCl: Ag ⁺	2.82	1.012	1.011
NaF: Ag ⁺	2.31	1.054	1.054

calculated with ICECAP for the Ag⁺-centred nearest-neighbour cluster embedded in a relaxed shell-model lattice, as a function of Ag⁺-anion separation. While substitutional Ag⁺ is off centre in RbCl, this feature is not reproduced by either our quantum-cluster or our shell-model descriptions, and is not allowed for here. In table 4 we give the equilibrium nearest-neighbour distance for Ag⁺ as calculated by ICECAP for the embedded quantum cluster, and as calculated by HADES with the derived potentials of table 2. The differences are very small. This result indicates that the host anion-anion interaction in the quantum cluster must be quite similar to that of the shell-model which replaces it in the HADES calculation.

We have tested the sensitivity and consistency of potentials derived by the method of § 2, by varying the input values of (A , ρ , C , α) in equation (1) and (2), for the case of Cu⁺ in KCl. We describe three cases: (i) with input parameters (5275.0 eV, 0.3 Å, 0.0, -13.0 eV); (ii) with α changed to -15.0 eV from case (i); (iii) with A changed to 3275.0 eV from case (ii). In each case the nearest-neighbour Cu⁺-Cl⁻ distance ranged between $0.94a$ and $1.06a$, where $a = 3.116$ Å is the perfect-lattice nearest-neighbour

Table 5. Cu^+-Cl^- shell-model, short-range potential derived from quantum clusters in KCl with different initial values for fitting procedure, cases (i), (ii), and (iii) (see § 3).

Case	A (eV)	ρ (Å)	C (eV Å ⁶)	α (eV)
(i)	7545.10	0.2977	411.29	-2.5
(ii)	5216.99	0.3173	491.93	-0.41
(iii)	14044.07	0.2726	334.90	-0.70

Table 6. Values of Buckingham potential $V(r)$ (equation (1)) at distances d for cases (i), (ii), and (iii) of table 5, and maximum variations ΔV . Units for V and ΔV : eV; units for d : perfect-lattice nearest-neighbour spacing a .

d	Case (i)	Case (ii)	Case (iii)	ΔV
1.06	-0.202	-0.220	-0.182	0.04
0.94	-0.249	-0.268	-0.228	0.04
0.71	+1.031	+0.746	+1.437	0.69

Table 7. Activation energy (eV) for Ag^+ diffusion by the collinear vacancy mechanism, calculated with Ag^+ -host anion potentials derived for different host crystals, from table 2.

System	Potential derived for					a (Å)
	RbCl: Ag^+	KCl: Ag^+	NaCl: Ag^+	AgCl	NaF: Ag^+	
RbCl: Ag^+	0.87	0.74	0.98	0.61	—	3.29
KCl: Ag^+	0.94	0.81	0.98	0.66	—	3.145
NaCl: Ag^+	1.01	1.04	0.92	0.75	—	2.82
NaF: Ag^+	—	—	—	—	0.71	2.31

spacing. The derived values of the parameters are given in table 5, where considerable variation is to be noted. In table 6, we give values of the corresponding Buckingham potential (1), at distances d of $0.94a$ and $1.06a$, spanning the range of values from which the parameters were derived, and also at $d = 0.71a$, which is approximately the distance at which the potential would be applied for a diffusion process. For each distance we give ΔV , the maximum variation among the three potentials (i), (ii), and (iii). The result is $\Delta V = 0.04$ eV at $d = 0.94a$ and $d = 1.06a$, which is within the tolerance of 0.05 eV from which we established the convergence criterion for the fitting procedure. However, for $d = 0.71a$, we see that $\Delta V = 0.69$ eV, a variation that could produce an unacceptably large discrepancy in a calculated activation energy. We conclude that although the method is consistent within the range of distances from which the results are derived, it cannot be relied upon for application well outside that range. We shall discuss this point in § 4.

In table 7 we give the activation energy for Ag^+ diffusion by the collinear vacancy mechanism as calculated by HADES using the potentials of table 2, derived for the Ag^+-Cl^- interaction in various crystals. This collinear activation energy is taken to be the difference between initial and activated configurations. The initial configuration is taken

to consist of a Ag⁺ ion substitutional at a host cation site, the origin, with a second-neighbour cation vacancy at coordinates (1, 1, 0) in units of a . Experimental values of a (Ashcroft and Mermin 1976) are also given in table 7. The activated configuration has the Ag⁺ impurity at the so-called saddle-point position, (0.5, 0.5, 0.0) a . We assume that our best value for the activation energy in a given crystal is given by the potential for that crystal, namely 0.87 eV for RbCl:Ag⁺, 0.81 eV for KCl:Ag⁺, 0.92 eV for NaCl:Ag⁺, and 0.71 eV for NaF:Ag⁺.

We have also investigated the non-collinear vacancy mechanism for diffusion. In this case activated configurations have the diffusing ion (Ag⁺) displaced in the z direction perpendicular to the xy plane defined above for the vacancy process. We find significantly lower activation energies for RbCl:Ag⁺ and KCl:Ag⁺, namely 0.44 eV and 0.51 eV, with Ag⁺ core z -coordinates of 0.35 a and 0.33 a , respectively. For KCl:Ag⁺ we have checked whether the activated configuration occurs with (x, y) coordinates different from 0.5, 0.5) a , and z different from zero, and we find that it does not. For NaCl:Ag⁺ and for NaF:Ag⁺, the collinear configuration gives the lowest activation energy. Thus, in summary, our calculated activation energies for Ag⁺ diffusion by the vacancy mechanism in RbCl, KCl, NaCl, and NaF are, respectively, 0.44, 0.51, 0.93, and 0.72 eV.

We are not aware of experimental data with which to compare these results. For NaCl:Ag⁺ and NaF:Ag⁺, they are similar to values obtained for cation self-diffusion in the alkali halides (Catlow *et al* 1979a), while for RbCl:Ag⁺ and KCl:Ag⁺ they are somewhat higher than that found for Ag⁺ in AgCl (Corish and Jacobs 1972), which is 0.28 eV. If one infers that our calculated values are too large, then this might be taken as supporting the idea of strong quadrupole deformability of Ag⁺, but any discrepancy may well be due in significant part to inaccuracy of the derived potentials in the activated configuration. We shall return to this point in § 4.

From table 7 we can assess the transferability of potentials by comparing calculated collinear activation energies for Ag⁺ in a given crystal, say RbCl, based on Ag⁺-Cl⁻ potentials derived from RbCl, KCl, NaCl, and AgCl. The results are respectively 0.87, 0.74, 0.98, and 0.61 eV, which represent variations of between 12% and -30%. Similar results are obtained for KCl and NaCl. In at least some cases the discrepancies would be unacceptable.

We have tested the sensitivity of the calculated activation energy by the collinear vacancy mechanism to two other features of our model, both for the case of Ag⁺ in NaCl. First, we have transferred the Ag⁺-Na⁺ potential derived by Catlow *et al* (1979b), for Na⁺ in AgCl, based on the electron gas approximation (Wedepohl 1967), with parameters $(A, \rho, C) = (9953.05 \text{ eV}, 0.210 \text{ \AA}, 0.0)$. These may be compared with values in table 1, obtained by the averaging process of equations (3a)-(3c). The calculated activation energy is 0.934 eV, which is to be compared with 0.926 eV from table 7, a difference of less than 1%. Our second test involves the lattice spacing, and is carried out again for NaCl:Ag⁺, using the Ag⁺-Na⁺ potential from AgCl:Na⁺. The host lattice spacing that we now use is in equilibrium with the host-lattice potential (Catlow *et al* 1981), namely 2.789 Å, whereas up to now we have used the experimental value of 2.82 Å, a difference of 1%. The calculated activation energy for Ag⁺ turns out to be 0.9567 eV, which compared with 0.934 eV, above, gives a difference of 2.4%. We conclude that our calculated results of table 7 are insensitive to our choices of Ag⁺-host cation potential and lattice spacing.

We now briefly describe the magnitude of distortions calculated for diffusion by the vacancy mechanism. In the initial configuration, halogen nearest-neighbours of the Ag⁺ ion are displaced by amounts that range up to 0.14 a (inward, in RbCl). In the collinear

Table 8. Activation energy (eV) for Ag⁺ and Cu⁺ diffusion by the interstitial mechanism, calculated with potentials from table 2, and from Meng *et al* 1988.

System	Energy
RbCl: Ag ⁺	1.01
KCl: Ag ⁺	0.83
NaCl: Ag ⁺	<0
NaF: Ag ⁺	<0
KCl: Cu ⁺	0.78
NaCl: Cu ⁺	<0

activated configuration, displacements of up to $0.26a$ occur adjacent to the saddle point (outward, in NaF). These displacements lie well outside the range from which the potentials were derived.

In table 8 we present results of calculations of the activation energies for interstitial diffusion of Ag⁺ and of Cu⁺. In the initial configuration the Ag⁺ ion is at the centre of a cube with alternating cations and anions at its corners. In the activated configuration it is at the centre of a face of that cube. In table 8, we note that in the host crystals with the smallest cation, namely Na⁺, the calculated activation energy is unphysical, that is, negative. For Ag⁺ and Cu⁺ in KCl, our calculated values of 0.83 and 0.78 eV respectively compare well with the experimentally deduced values of Pershitz *et al* (1981), namely 0.95 and 0.83 eV, respectively. The potential used for Cu⁺ in KCl is from our previous work (Meng *et al* 1988). We comment on these results in § 4. The calculated configurations contain quite strong distortions, ranging up to 29% of the perfect lattice spacing for nearest-neighbour K⁺ ions in the activated configuration of KCl: Cu⁺.

4. Discussion

Some results of this work are qualitative. They show that within the range of distortions from which impurity potentials are derived, they are consistent (table 4). Table 6 illustrates how such potentials may be unreliable when they are applied in configurations that differ strongly from those used in deriving them, because potentials that are equivalent in the range of derivation may differ markedly outside that range.

The calculated activation energies for Ag⁺ diffusion by the vacancy mechanism lack direct experimental comparison. They fall into two classes. In host lattices with small cations, NaCl and NaF, the activation is collinear, and the energies are respectively 0.93 and 0.72 eV, these being comparable to cation self-diffusion values in these crystals. In host lattices with larger cations, RbCl and KCl, the activation is non-collinear, and the energies are respectively 0.44 and 0.51 eV, significantly larger than the corresponding Ag⁺ self-diffusion value in AgCl. The calculated activation energies for Ag⁺ and Cu⁺ diffusion by the interstitial mechanism could not be obtained for NaCl and NaF, but in KCl they compare reasonably with experiment: respectively 0.83 and 0.78 eV, against 0.95 and 0.83 eV. The calculated value of 1.01 eV in RbCl therefore also seems reasonable.

What then are the prospects for simulating diffusion processes with shell-model impurity potentials derived from quantum clusters? For the Ag⁺ impurity considered here, one could incorporate the quadrupole deformability introduced by Jacobs *et al*

(1980). This would lower the calculated Ag⁺ diffusion activation energies, which for the interstitial mechanism is already low compared to experiment. It is apparently not applicable to Cu⁺. The absence of experimental data with which to compare calculated vacancy-mechanism activation energies mean that the present results remain inconclusive. However, the model used here could be improved. We believe that an important improvement is a more accurate derivation of the short-range Ag⁺-host anion potential. For application to processes such as diffusion, the derivation should include compression of the quantum cluster of up to 30%. A spline-fit potential rather than the simple Buckingham form of (1) would probably be required. When such large distortions of the quantum cluster are used, reasonably flexible basis sets (as opposed to the fully-contracted minimal sets used here) will be required in order to obtain an accurate potential. It may be necessary to derive the shell-model dipole and quadrupole deformability parameters for the Ag⁺ ion from the quantum-cluster calculations, rather than to transfer them from another crystal. The same can be said for second-neighbour impurity-host potentials. All of these improvements are feasible. However, there is no guarantee that they will be sufficient to provide accurate results. Specifically, if many-body inter-ionic effects are significant, then pair potentials will be inadequate, however accurately they are derived.

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