

## THEORY OF HYDROGEN IN LIQUID AND SOLID METALS\*

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### Summary

A method for calculating the interatomic forces between isolated hydrogens and their host metal atoms is outlined. The method uses a semi-empirical, molecular-orbital approach for a suitable cluster of atoms, with the empirical parameters fitted to experimental potential energy curves for diatomic molecules. Parameters suitable for hydrogen in liquid or solid Li and Na are given.

The method is applied to the calculation of solvation energies of hydrogen in liquid Li and Na, where satisfactory agreement with experiment is obtained. Detailed potential energy surfaces are also found for H in solid Na and estimates are made of local mode frequencies, the stability of the tetrahedral sites, lattice relaxation, and effective charges, and atomic radii. Neither the anionic nor the protonic limit is appropriate. It has not proved possible to describe the potential energy surfaces in terms of a sum of two-body and volume-dependent terms alone.

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### 1. Introduction

Many properties of hydrogen in metals depend on the interatomic forces between the hydrogen and the host atoms. Such properties include local mode frequencies, interstitial site occupancies and diffusion behaviour. In the present paper we discuss the results of calculations on the interactions of hydrogen with alkali metals.

There are two main approaches to the theory of hydrogen in metals. One is the band structure approach, which exploits the periodic structure of the host metal and its hydrides [1]. This is particularly suitable for studies of the electronic properties of ordered hydrogen-metal systems, but does not readily give interatomic forces for, say, an isolated hydrogen moving in a single interstice. The other approach studies a small cluster of metal atoms and a hydrogen by molecular methods, calculating the total

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energy for various geometries. This exploits the relatively short range of most chemical effects. In its simplest form (*e.g.*, ref. 2), only a single metal atom,  $M$ , and a hydrogen are considered, and the interactions in a solid are then treated as a superposition of two-body forces. We go beyond this simplifying assumption in the present work, treating a variety of clusters  $M_NH$  appropriate to solid and liquid alkali metals.

*Ab initio* molecular orbital methods, whilst excellent for small systems (usually two or three atoms only, except in special cases), become complex and expensive for many practical systems. We shall cite some results for Li, for example, but we could not expect to deal with a  $Ta_NH$  cluster by full Hartree–Fock theory. Thus, we have turned to approximate molecular-orbital methods, although we use them in a slightly modified form. The virtue of the approximate methods is that most of the physical ideas are retained, while some of the more complex steps are simplified by making suitably-parameterised approximations. The essence of our approach is to obtain parameters suitable for estimates of interatomic forces by making sure that the same parameters describe well the known forces in simple, related molecules. Loosely speaking, we use the approximate method as an extrapolation procedure from experimental data rather than as an approximation to *ab initio* theory.

The molecular approach to metallic systems is, of course, very different from the conventional view based on electron gas theory. It should be stressed that, despite the differences in formalism, the physics of the two approaches is much the same and the qualitative predictions have much in common. Screening is included in both approaches, but in a different manner; for example, the biggest difference is in the extent to which geometric factors are included.

## 2. The molecular orbital method

### 2.1 The CNDO method

We have concentrated on the CNDO (Complete Neglect of Differential Overlap) method in the present work. This is one of a class of semi-empirical methods [3] which has the advantage of being simple and easily modified, without sacrificing physical sense. It has also been used for other condensed-matter systems with some success [4]. Standard parameterisations exist for first- and second-row atoms which predict the electronic structure, bond lengths and geometries quite well [3] but, as stressed in Section 1, the parameters must be revised for the systems and properties of interest here.

The CNDO method approximates the Hartree–Fock–Roothaan equations by neglecting terms of the order of the overlap between orbitals on different atoms, and by approximating other matrix elements systematically [3]. A basis set of Slater orbitals is used for the outer electrons on each atom:  $1s$  orbitals for H,  $2s$  and  $2p$  for Li, and  $3s$ ,  $3p$  and  $3d$  for Na. The same orbital exponent is used for each orbital on a given atom. Basically,

three types of parameter must be fixed. If  $A, B$  label the different atomic species, and  $\mu, \nu$  the atomic orbitals, these are:

(a) Orbital Exponents. These determine the overlaps,  $S_{AB\mu\nu}$ , which are used in expressions for off-diagonal matrix elements, plus the Coulomb terms  $\gamma_{AA}, \gamma_{AB}, \gamma_{BB}$ , which determine the electron-electron and nuclear attraction integrals.

(b) Ionisation Potential ( $I_{A\mu}$ ) and Electron Affinity ( $A_{A\mu}$ ). These enter in the combination  $(I_{A\mu} + A_{A\mu})/2$ , and determine the relative attraction for electrons of the different species.

(c) Bonding Parameters,  $\beta$ . The degree of bonding is fixed by resonance-type integrals,  $\beta_{AB}^0$ , which are assumed to have the form:

$$\beta_{AB}^0 = \frac{K}{2}(\beta_{AA}^0 + \beta_{BB}^0) \quad A \neq B, \quad (1)$$

where  $K$  is a further parameter to be determined.

Given values for the various parameters, the CNDO program obtains self-consistent solutions analogous to the Hartree-Fock solutions. These list one-electron energy levels, the total energy, the wavefunctions, and an "effective charge" for each atom. If  $c_{ij}$  is the weight of atomic orbital,  $i$ , in eigenfunction,  $j$ , then the effective charge is:

$$Q_A = \left\{ -2 \sum_{\substack{\text{occupied} \\ \text{orbitals} \\ j}} \sum_{\substack{\text{atomic} \\ \text{orbitals } i \\ \text{on site } A}} |c_{ij}| + Z_c \right\} |e| \quad (2)$$

$Z_c$  being the charge of the nucleus and core electrons; the factor 2 occurs because of spin. One should beware of attaching too much significance to  $Q$ , for there is still some arbitrariness. For example,  $Q_A$  changes, even at constant charge density, if the basis orbitals are altered. But the effective charge is a useful guide.

## 2.2 Parameterisation

Since we wish to use the CNDO method to calculate energies as a function of atomic position, it is important to fix the parameters from data as similar as possible. To this end, we fit the most sensitive parameters from experimental potential energy data for the molecules  $M_2$  and  $MH$ . The results are listed in Table 1.

The orbital exponents for the nodeless Slater orbitals were taken as 1.2 for hydrogen [3], and as 0.6396 (Li) and 0.836 (Na) from ref. 5. The term in the ionisation potential and electron affinity was slightly modified from the free atom values, following Baetzold [6]. However, the changes are modest, and should have no notable effect on charge densities. The  $d$  orbitals on Na proved to be largely superfluous, and were omitted from the more detailed calculations.

The bonding parameters,  $K$  and  $\beta_{AA}^0$ , prove to be the most critical parameters. We obtained the  $\beta_{AA}^0$  by making the predicted  $M_2$  potential energy

TABLE 1

CNDO parameters

Species	Orbital exponents $\zeta$ (a.u. <sup>-1</sup> )		Orbital electronegativities + $(I_\mu + A_\mu)/2$ (eV)		Bonding parameters	
	<i>s</i>	<i>p</i>	<i>s</i>	<i>p</i>	$\beta^0$ (eV)	<i>K</i>
Na	0.836	0.836	2.57	1.52	-0.99	1.063
H	1.2	—	7.1761	—	-9.0	—
Li	0.6396	0.6396	3.1055	1.258	+1.818	1.754

curve agree as closely as possible with a potential fitted to experimental data [7]. The parameter *K* of eqn. (1) was then adjusted to make the predicted MH potential energy curve agree with corresponding experimental data. The results are shown in Fig. 1. Generally, agreement with the equilibrium position is excellent, and the harmonic and leading anharmonic parts of the potential near equilibrium, are also well reproduced. The predictions generally lie between the two "experimental" curves, showing that we have achieved agreement to within the accuracy of our knowledge of these interactions. Only at large distances does agreement become poor, partly because the CNDO method does not give the correct separation limit, and partly because of convergence problems.

Since the parameters have been fixed from potential energy data, there is no reason, *a priori*, why the same parameters should predict other properties well. It is, however, worth stressing that the parameters do appear to give good charge densities. The results of Fig. 1 suggest this, for charge densities are the main factor in determining energy surfaces [8]. More direct evidence has been obtained, however, by comparing the charge density in a cluster from CNDO with Hartree-Fock cluster calculations [9] and with self-consistent KKR and pseudoatom calculations for Li [10]. The general agreement is good, both qualitatively and quantitatively. It will be discussed in more detail elsewhere. Finally, we remark that our parameters are appropriate to isolated hydrogens in alkali metals. It is known from work on other systems [4] that parameters for ionic systems (*e.g.*, the crystalline Li-H and Na-H hydrides) must be derived separately.

### 3. Hydrogen in liquid metals

When an impurity like hydrogen dissolves in a liquid metal, one would expect its chemical effects to be confined to a few immediate neighbours. The interaction of the hydrogen with these neighbours will favour certain geometric configurations, so that the impurity will usually be surrounded by atoms in some specific arrangement. So far as the remaining atoms in the liquid are concerned, however, it is largely immaterial whether such a grouping

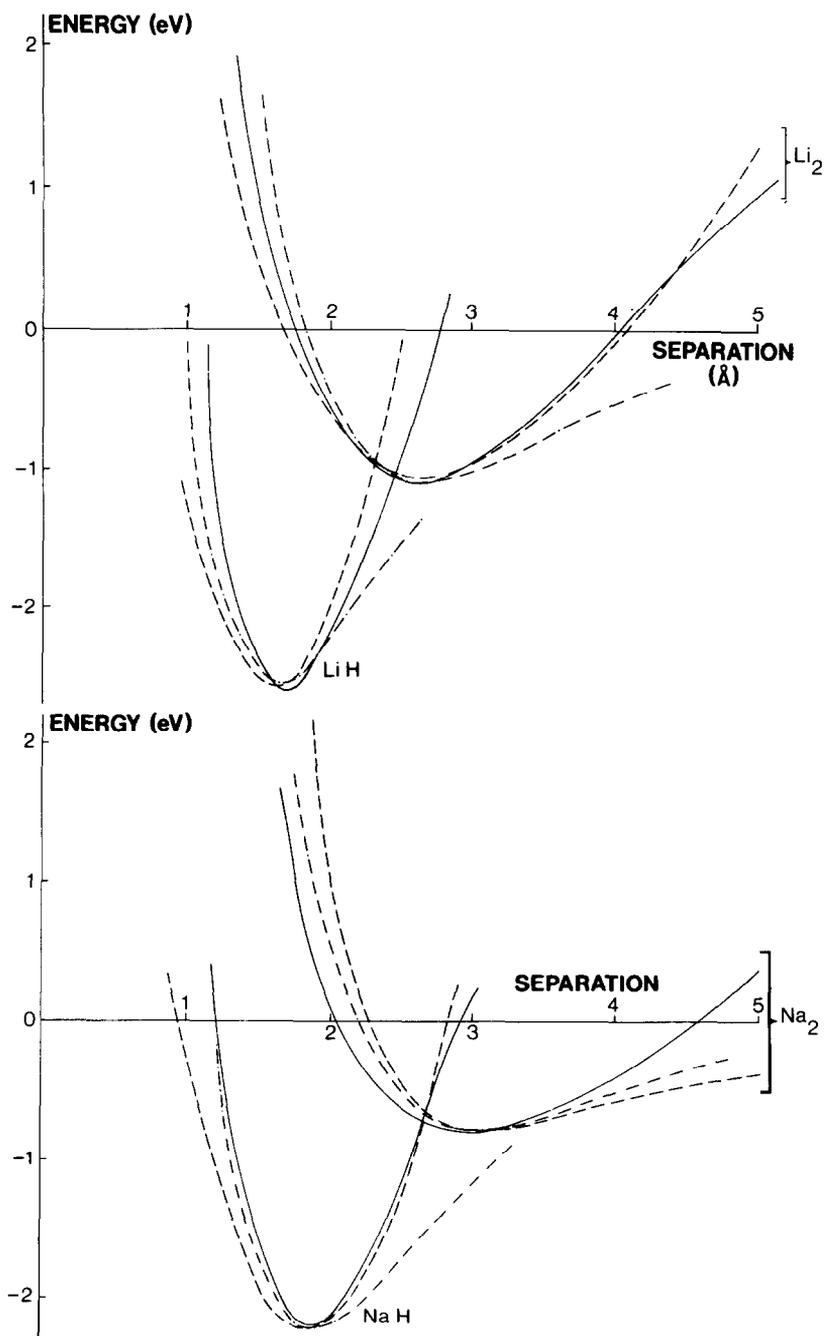


Fig. 1. Potential energy curves for diatomic molecules, LiH, Li<sub>2</sub>, NaH, Na<sub>2</sub>. The full lines give the CNDO fit, and the broken lines give two fits consistent with experimental data: --- Simple Morse potential fitted to the lowest frequency and leading anharmonic corrections, with a constant term added to give the correct depth of minimum. - · - · - Generalised Morse potential, fitted to give the correct binding as well as the lowest frequency and leading anharmonic corrections.

TABLE 2

## Solvation energies at constant volume

The results here are for tetrahedral clusters,  $T_0$ , with M-H spacing  $x_0$ , supplemented where stated by a further tetrahedron  $T_x$ . The metal atoms in  $T_x$  have a M-H spacing,  $x$ , and lie above the centres of the faces of  $T_0$ . For the spacings,  $x$ , marked, \*, the atomic radii of Section 3 imply that the atoms in  $T_0$  and  $T_x$  are just in contact.

System	$x_0$ (Å)	$x$ (Å)	Solvation energy (eV)	Charge on H  e
Li ( $T_0$ )	2.2	—	-3.72	-0.44
( $T_0 + T_x$ )	2.2	4.0	-4.70	-0.43
( $T_0 + T_x$ )	2.2	3.65	-3.89	-0.45
( $T_0 + T_x$ )	2.2	3.36*	-3.34	-0.46
(Expt. [13, 14])	—	—	-4.43(H), -4.29(D)	—
Na ( $T_0$ )	2.35	—	-4.11	-0.25
( $T_0 + T_x$ )	2.35	4.0	-2.99	-0.26
( $T_0 + T_x$ )	2.35	3.65	-2.82	-0.23
( $T_0 + T_x$ )	2.35	3.41*	-2.76	-0.24
(Expt. [12])	—	—	-3.74	—

TABLE 3

## Solvation energies at constant pressure and volume

Results are for a single tetrahedron of metal atoms and are in eV.

	$Li_4H$	$Na_4H$
Constant pressure (up to $10^4$ atm)	-3.58	-3.96
Constant volume	-3.72	-4.11
Experiment	-4.43(H), -4.29(D)	-3.74

of atoms has a hydrogen in their midst or not. In other words, solvation energies can be calculated by comparing the energies of isolated clusters of metal atoms with, and without, associated hydrogens. Thompson has described the basic principles of such calculations [11]. We shall follow his methods in many features, but using our more advanced CNDO method.

Calculations for liquids contain features which do not arise in solids because of the variety of possible local atomic arrangements. We have made two different sorts of cluster calculation:

(a) "Constant volume". Here one chooses a particular arrangement of metal atoms, *e.g.*, tetrahedral, and alters their spacing to obtain a minimum energy with a hydrogen at the centre. The total energy is then compared with that for the metal atoms at the same positions, but without the hydrogen present.

(b) "Constant pressure". Here one plots the total energy of clusters with, and without hydrogen as a function of spacing, and compares energies

at points where the two curves have equal gradients. In addition, energies have been obtained for several different types of cluster, namely, linear, triangular, tetrahedral, and octahedral arrangements. In all cases, the tetrahedral arrangement was favoured, giving the greatest binding of the hydrogen. The results for the tetrahedral clusters were also supplemented by calculations for larger clusters in which a further four metal atoms were included.

The results are listed in Tables 2 and 3. Table 2 shows that the solvation energies at constant volume agree quite well with those observed. The addition of an outer tetrahedron of atoms produces a significant effect, without altering the broad orders of magnitude. As the outer tetrahedron is moved away from the central hydrogen and from contact with the inner metal atoms, the agreement with experiment improves marginally. Table 3 shows that the differences in solvation energy between the constant volume and constant pressure cases are modest, the constant pressure ones being smaller in magnitude. These have only been compared for the tetrahedral cluster.

Other incidental results to emerge are effective radii for the three species, determined from the equilibrium geometries of the  $M_4$  cluster (giving 1.675 Å for Li and 1.715 Å for Na) and  $M_4H$  clusters (giving values for hydrogen of 0.525 Å in Li and 0.535 Å in Na). Effective charges are listed in Table 2, as defined in eqn. (2). These confirm that the hydrogen is present in neither the protonic nor the anionic extreme, but appears to be somewhere between the atomic and anionic limits. The charge is relatively insensitive to the local environment.

#### 4. Hydrogen in solid alkali metals

One of the aims of the present work is to understand the main qualitative features of the potential energy surface in metals. For example, one wants to know whether there is only one type of stable site, whether there are metastable subsidiary potential minima, and whether the total energy can be written as a sum of two-body terms. The question of subsidiary minima is particularly important in b.c.c. transition metals, notably V, Nb, and Ta. Neither the present work, nor other current theoretical approaches, appear capable of giving total energies accurate to the order of 0.01 - 2 eV needed in detailed applications, even for triatomic molecules and with extensive configuration admixture [15]. In practice, therefore, one would expect calculations such as the present ones to be used to give as much qualitative and semi-quantitative information as possible, and then to be refined by use of experimental data (like local mode frequencies) before use in, say, diffusion calculations. In the case of Na:H there are no useful data with which to compare our results, but it will appear that the conclusions are reasonable in nature and magnitude. The calculations should be regarded as preliminary for work on the more complex, but important, transition-metal systems.

TABLE 4

Cluster of Na atoms and interstitial sites

Atom	Basis orbitals included	Position*	Number of equivalent sites
Na	2s, 2p	0, $\pm\frac{1}{2}$ , 0 (sites A, B)	2
Na	2s, 2p	$\pm\frac{1}{2}$ , 0, $\pm\frac{1}{2}$ (sites C,D,E,F)	4
Na	2s	$\left\{ \begin{array}{l} \pm 1, \pm\frac{1}{2}, 0 \\ 0, \pm\frac{1}{2}, \pm 1 \end{array} \right\}$	8
Na	2s	$\pm\frac{1}{2}, \pm 1, \pm\frac{1}{2}$	8
Octahedral sites		0, 0, 0	1
		$\left\{ \begin{array}{l} 0, 0, \pm\frac{1}{2} \\ \pm\frac{1}{2}, 0, 0 \end{array} \right\}$	4
Tetrahedral sites		$\left\{ \begin{array}{l} 0, 0, \pm\frac{1}{4} \\ \pm\frac{1}{4}, 0, 0 \end{array} \right\}$	4

\*Units are  $a = 4.28 \text{ \AA}$ 

We have calculated a potential energy surface for hydrogen in a cluster of 22 sodium atoms. The hydrogen lies at the centre of the b.c.c. array listed in Table 4. Because of the high symmetry, almost all the important features can be obtained from the contours over the square defined by the four second neighbours to a given octahedral site (CDEF in the Table). The important octahedral and tetrahedral sites are also listed.

The calculations show that the *tetrahedral* sites are favoured, being stable by about 0.25 eV over the unstable octahedral sites. The energy barriers between tetrahedral sites (*not* to be confused with activation energies for diffusion) are lowest *via* the octahedral sites, the most direct path having a 0.30 eV barrier. Relaxation of the four nearest neighbours to the tetrahedral site to minimise the energy, only leads to a lowering of 0.003 eV. The distortions are small, involving an inward motion of the sodiums. Thus, that at  $(X, Y, Z) \equiv (a/4, 0, a/2)$  relative to a tetrahedral site, moves to  $(0.9817 X, Y, 0.9813 Z)$ , *i.e.*, motions of between one and two percent. This suggests an "effective radius" of about 0.49 Å, marginally smaller than in the liquid state. The effective charges of eqn. (2) are again in between the protonic and anionic extremes, being  $-0.3 |e|$  for the tetrahedral site and  $-0.24 |e|$  for the octahedral site. Another effective charge can be defined from the change in dipole moment per unit displacement. This other charge is a tensor, in general. For displacements along the tetragonal axis of the tetrahedral site a value of  $-1.3 |e|$  is obtained.

The potential well near the tetrahedral site is highly anharmonic. Indeed, if one fits only the harmonic part of the energy surface very close to the minimum local mode, energies of 0.63 eV (motion along tetragonal axis) and 2.31 eV (motion normal to axis) are predicted, and the zero-point

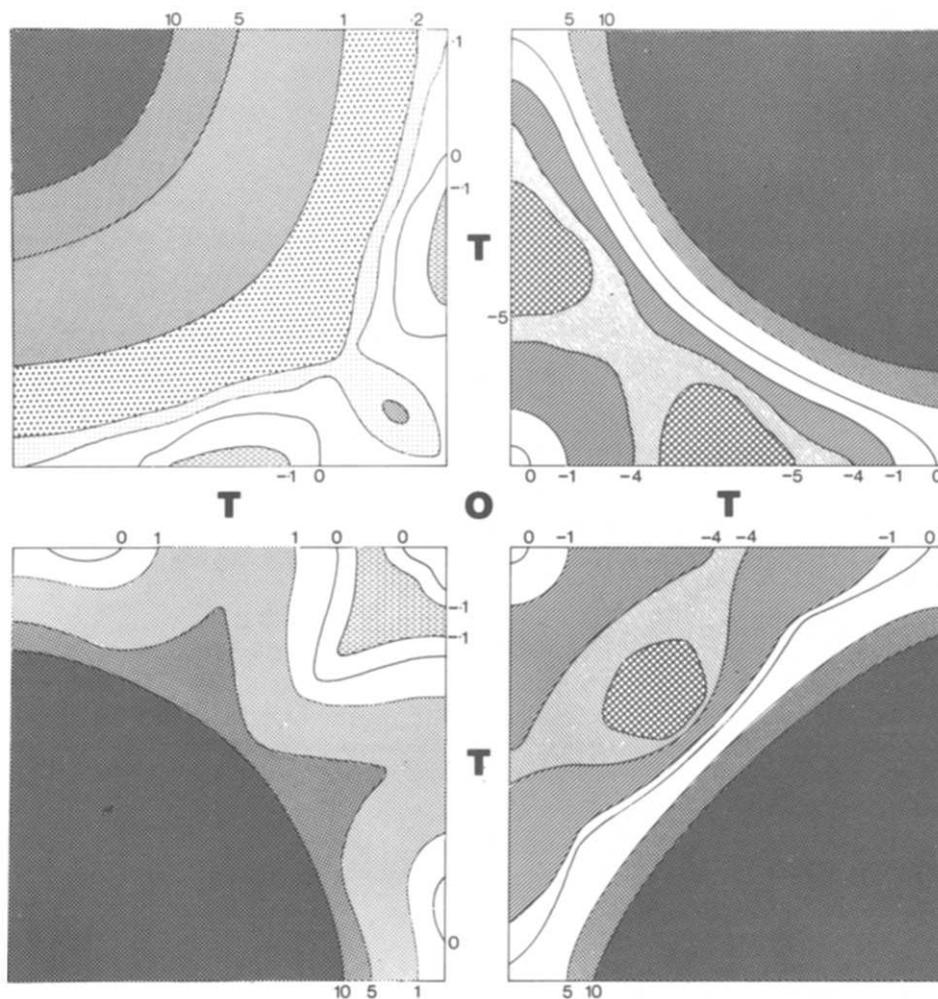


Fig. 2. Potential energy surface for H in the  $\text{Na}_{22}$  cluster. Octahedral sites are at centres of the edges; the tetrahedral sites are on the axes of the square, midway between the centre and the edge. Four approximations are shown:

- (a) Upper left quadrant: CNDO cluster calculations.
- (b) Lower left quadrant: sum of 2-body CNDO interactions.
- (c) Lower right quadrant: sum of 2-body Morse potentials.
- (d) Upper right quadrant: sum of 2-body Generalised Morse potentials.

Energies have been normalised to be equal at the octahedral site, 0, and areas above certain contours are distinctively shaded. The lowest energies have the dashed shading (*i.e.*, not dots nor cross-hatching).

energy would exceed the barrier between sites. A simple variational calculation for the anharmonic well gives a zero-point energy of around 0.09 eV, with excitation energies of 0.08 eV (motion along axis) and 0.22 eV (motion normal to axis). These values are much closer to observed local mode ener-

gies of substitutional hydrogen in ionic crystals and to observed energies of hydrogen in other metals. However, the values are large when one recalls the barrier of only 0.25 eV between sites: there is probably only one excited vibrational state lying below the top of the lowest barrier.

Detailed energy contours are shown in Fig. 2. We have been unable to fit them by any two-body potential. In particular, sums of the Morse, generalised Morse, or CNDO two-body terms of Fig. 1 do not provide a good fit. This can be seen from Fig. 2. There are many differences in detail and, of the sums of two-body terms, only the generalised Morse form predicts a minimum energy for the tetrahedral site. In this respect, our conclusions differ from the results of Kunz *et al.* [16] obtained by a rather different method on the hydrogen-lithium surface system.

## 5. Conclusions

We have used semi-empirical molecular orbital methods to deduce the energies of a range of clusters of alkali metals and hydrogen. These calculations are intended to give potential energy surfaces for diffusion and other properties. The important parameters deduced are the CNDO parameters in Table 1, for the potential energy surface does not resolve easily into the conventional two-body forces. Instead, the situation is analogous to pseudopotential theory, where one can calculate properties straightforwardly given pseudopotential parameters; here the CNDO parameters define the properties of interest in a similar way.

The work on alkali metals was intended as a preliminary to studies of the more important transition-metal systems. It is gratifying, therefore, that reasonable values for solvation energies have been obtained, and that the results for both solid and liquid host metals appear reasonable.

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