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Repulsive Interactions for LiH†

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The cohesive energy, inter-ionic distance, and compressibility have been obtained for the LiH crystal employing a point-ion model with repulsive two-body interactions calculated by the Heitler-London method. Results are presented and compared for screened hydrogenic, two-electron open-shell, and Hartree-Fock wave functions for the Li^+ and H^- ions. Interactions obtained by a semiclassical method of calculation are also presented and compared with the diatomic quantum-mechanical results.

I. INTRODUCTION

The Born model has been used for many years to calculate physical properties of ionic crystals.[1] This approach, which consists in considering energy terms arising from interactions between pairs of ions, has been extended to the consideration of point defect states of these systems.[2] A critical step in all of these calculations is the determination of the overlap repulsive forces between pairs of host ions and especially between a host ion and a defect atom or molecule. In the work reported on here, theoretical approaches are used rather than an empirical fitting of these interactions to crystal data.

In Sec. II the Heitler-London method has been employed to calculate the repulsive interactions between pairs of rigid two electron atoms and ions. These interactions are then used to construct models of both pure and defect states of the LiH crystal. This crystal was chosen as only four electrons are involved in a diatomic calculation and therefore, results may be compared for a number of different possible choices of the Li^+ and H^- ionic wave functions. Functions employed in various earlier quantum-mechanical calculations[3–6] on LiH have been considered. LiH was chosen also because proposed models can be compared with a considerable body of experimental data.[7] Finally, radiation damage studies have been carried out on this crystal in recent years[8] and the method used here to obtain repulsive interactions is readily applied to theoretical calculations of the properties of the point defects produced by radiation effects.

Semiclassical methods for obtaining interactions between homonuclear atoms have been developed by Firsov,[9] by Abrahamson *et al.*,[10] by Abrahamson,[11,12] and by Wedephol.[13] These methods, which employ statistical electron distributions, should have the greatest validity for heavy atoms and ions. However, Abrahamson has calculated interactions between pairs of light atoms and has found reasonable agreement with experiment.[11,12] In Sec. III the method of Wedepohl is generalized to include heteronuclear interactions and is applied to the problem of LiH. The results are compared with the diatomic quantum mechanical calculations.

II. QUANTUM-MECHANICAL INTERACTIONS

A. Method

Curves of net interaction energy versus internuclear distance for a pair of rigid atoms or ions were obtained by calculating the total energy $E(R)$ as a function of internuclear distance R and subtracting the total energy $E(\infty)$ of the separated pair. To obtain the repulsive interaction $E_{\rm rep}$, the Coulomb energy of the pair of ions, Q_aQ_b/R was also subtracted, with the result

$$E_{\rm rep}(R)=E(R)-E(\infty)-Q_aQ_b/R. \qquad (1)$$

Here Q_a and Q_b are the net charges on ions a and b.

The energy $E(R)$ is calculated from the usual expression

$$E(R)=\int\psi^*H\psi d\tau\,, \qquad (2)$$

where, in atomic units,

$$H=-\tfrac{1}{2}\sum_i\nabla_i^2-\sum_{i,a}\frac{Z_a}{r_{ia}}+\sum_{i>j}\frac{1}{r_{ij}}+\frac{Z_aZ_b}{R}\,. \qquad (3)$$

This Hamiltonian H for the diatomic systems considered contains the usual electronic kinetic energy,

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[1] An extensive collection of references may be found in an article by M. Tosi, Solid State Phys. **16**, 1 (1964).

[2] References may be found in the review article by L. W. Barr and A. B. Lidiard, in *Physical Chemistry: An Advance Treatise* (Academic Press Inc., New York, to be published); see also, for example, R. D. Hatcher and G. J. Dienes, Phys. Rev. **134**, A214 (1964).

[3] E. A. Hylleraas, Z. Physik **63**, 771 (1930).

[4] S. O. Lundquist, Arkiv Fysik **8**, 177 (1954).

[5] R. P. Hurst, Phys. Rev. **114**, 746 (1959).

[6] D. W. Hafemeister and J. D. Zahrt, J. Chem. Phys. **47**, 1428 (1967).

[7] C. E. Messer, U. S. Atomic Energy Commission Report NYO-9470, 1960 (unpublished).

[8] F. E. Pretzel, D. T. Vier, E. J. Szklarz, and W. B. Lewis, Los Alamos Scientific Laboratory Report No. LA2463 (unpublished).

[9] O. B. Firsov, Zh. Eksperim. i Teor. Fiz. **33**, 696 (1957) [English transl.: Soviet Phys.—JETP **6**, 534 (1958)].

[10] A. A. Abrahamson, R. D. Hatcher, and G. Vineyard, Phys. Rev. **123**, 538 (1961).

[11] A. A. Abrahamson, Phys. Rev. **130**, 693 (1963).

[12] A. A. Abrahamson, Phys. Rev. (to be published).

[13] P. T. Wedepohl, Solid State Commun. **4**, 479 (1966).

TABLE I. Born-Mayer parameters, interionic distance, and cohesive energy for the first nearest-neighbor interactions only. Screened hydrogenic functions, δ = screening parameter.

	$\delta=0.6875$	$\delta=0.7208$	$\delta=0.82$	$\delta=0.90$	$\delta=0.95$	Hartree-Fock[a]	Hurst crystal[b] open shell
A in eV/molecule	145.78	155.48	203.48	257.38	293.26	90.676	105.60
B in Å^{-1}	2.5412	2.6371	2.9635	3.2360	3.3968	2.1012	2.4787
r_0 in Å	2.478	2.403	2.213	2.091	2.026	2.643	2.361
U in eV/ion pair	−8.54	−8.81	−9.63	−10.25	−10.61	−8.36	−8.83

[a] Reference 15. [b] Reference 5.

electron-nuclear, electron-electron, and nuclear-nuclear operators. The wave function ψ is expressed as a linear combination of Slater determinants of one-electron functions. In this work, the one-electron functions were represented by linear combinations of Slater functions of the form $\exp(-\delta r)$. No attempt is made at this stage to apply a variational principle to an energy expression as none of the energies discussed here is the total energy of a physical system. Instead, wave function parameters are varied until the repulsive interactions obtained from the corresponding charge distributions result in a good fit to crystal data. The one and two center integrals over Slater functions required in (2) were calculated with the Harwell Laboratory version of the Corbato-Switendick program DIATOM[14] further modified by the authors for the CDC 6600 computer.

The cohesive energy $U(R)$ was calculated as a function of interionic distance R from the expression

$$U(R)=6U_{\mathrm{rep\ I}}(R)+6U_{\mathrm{rep\ II}}(R)-\alpha e^2/R, \tag{4}$$

where α is the Madelung constant for the NaCl structure, e is the electronic charge, and $U_{\mathrm{rep\ I}}$ and $U_{\mathrm{rep\ II}}$ are the pairwise repulsive interactions for first neighbor Li^+-H^- and second nearest neighbor H^--H^-, respectively, obtained by fitting $E_{\mathrm{rep}}(R)$ to Born-Mayer or other appropriate analytic forms. The Li^+-Li^+ repulsion was, as expected, negligible at the second neighbor distance.

The equilibrium value for the interionic separation R_0 and the corresponding compressibility K were obtained from the relations

$$\left.\frac{dU}{dR}\right|_{R=R_0}=0 \tag{5}$$

and

$$\frac{1}{K}=\frac{1}{18R_0}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}, \tag{6}$$

respectively.

B. Results

The Li^+-H^- repulsive interaction E_{rep}, was calculated for three different sets of wave functions with the results shown in Fig. 1. When closed-shell free-ion one-electron functions which are close to the Hartree-Fock limit are used for both H^- and Li^{+}[15], the curve labeled "Hartree-Fock" was the result.[15] Substitution of two-electron open-shell functions of the form

$$\psi\sim\exp(-Z_1r_1-Z_2r_2)+\exp(-Z_1r_2-Z_2r_1)$$

used by Hurst[5] in his calculation of form factors for the LiH crystal yielded the curve marked "Hurst." Finally, closed-shell screened hydrogenic functions of the form $e^{-\delta r}$ were used as the one-electron functions with an adjustable screening parameter δ_H for the negative hydrogen ion only.[16] These curves are well represented by the Born-Mayer form $E_{\mathrm{rep}}(R)=A\ e^{-BR}$. Values of A and B for some of the wave functions used are presented in Table I. Examination of Fig. 1 shows that the Hartree-Fock free-ion H^- function, which leads to the most extended charge distribution for this ion of all those considered, results in the strongest overlap repulsion. The open-shell Hurst function yields an interaction almost identical to the one obtained with the screened hydrogenic function with screening parameter $\delta_H=0.75$.

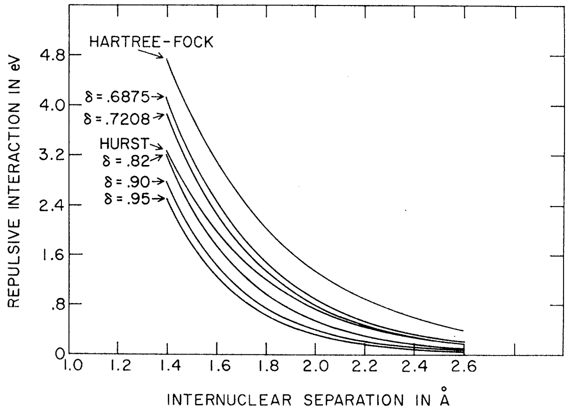

FIG. 1. Li^+-H^- repulsive interactions for various H^- wave functions.

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[14] F. J. Corbato and A. C. Switendick, in *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. II. One of us (C. R. F.) is indebted to Dr. D. Rimmer for supplying him with the Harwell version of the program DIATOM.

[15] The authors are indebted to Dr. A. W. Weiss and Dr. H. D. Cohen for supplying them with Hartree-Fock functions for the H^- ion. The Li^+ functions were taken from C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[16] Actually, it is only the H^- wave function that is considered to be adjustable. The Hurst (Ref. 5) and Lundquist (Ref. 4) results as well as calculations carried out in the course of this work all indicate that the Li^+ wave function in the LiH crystals should be taken to be the free Li^+ wave function.

TABLE II. Born-Mayer parameters for second nearest-neighbor interactions. Crystal parameters for first- and second-nearest-neighbor interactions. Screening parameter of the H^- ion.

	0.6875	0.7208	0.82	0.90	0.95
A (eV/molecule)	−13.4998	−7.7254	9.0797	29.2805	49.735
B in Å^{-1}	1.8101	2.3940	1.5297	1.8819	2.0859
r_0 in Å	2.423	2.397	2.303	2.216	2.160
U in eV/ion pair	−8.69	−8.83	−9.22	−9.68	−9.99
K (10^{-12} cm^2/dyn)	3.70	3.43	2.79	2.22	1.92

Second neighbor H^--H^- "repulsive" interactions were obtained for all the wave functions corresponding to the cases of Fig. 1. Several cases are presented in Fig. 2. Some of these interactions are actually attractive, which is consistent with the results of Hylleraas[3] and of Lundquist[4] for this system. The Hartree-Fock free-ion H^- function, which as noted above leads to the most diffuse charge distribution, yields the greatest attraction while the most contracted H^- function, the screened hydrogenic with $\delta = 0.95$ results in the greatest repulsion.

Using the values of the first neighbor interactions in Eqs. (4) and (5) yields the values of the interionic distance and cohesive energy listed in Table I. The values of the interionic distance, cohesive energy, and compressibility for first- and second-neighbor interactions are given in Table II for the screened hydrogenic wave functions. The strongest H^--H^- interaction changes the values of R_0 and U by only 6% compared to those for first neighbors only. The experimental values are $R_0 = 2.0415$ Å,[7] $U = -9.44$ eV/ion pair,[17] while values between 2.88×10^{-12} cm^2/dyne and 4.38×10^{-12} cm^2/dyne have been reported for the compressibility.[18]

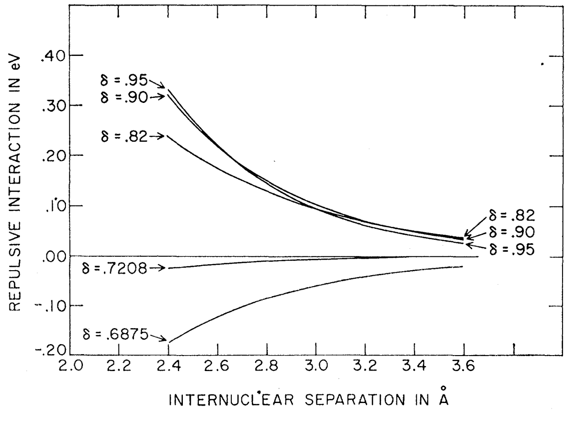

FIG. 2. H^--H^- "repulsive" interactions for various values of the screening parameter when screened hydrogenic functions are used for the H^- ion.

C. Discussion

Molecular interactions for LiH have been calculated by Varshni and Shukla[19] and by Hafemeister and Zahrt.[6] There is a difficulty in applying them to the crystal because of the different bonding present. In the present calculation this difficulty was overcome by considering the nature of the crystal and evaluating the interactions by the quantum-mechanical method employed. When interactions involving the defects are needed a model specifying the ionic charge distributions for the host lattice is particularly useful. The fitting of the H^- wave function to LiH crystal parameters results in an ion which has contracted considerably compared with the free ion. This result is in general agreement with the work of Hurst[5] and Lundquist.[4] The diatomic calculation reported here provides a model for the H^- ion for calculations of the interactions between point defects and the host lattice. Additionally, for a defect calculation which involves large relaxations of the ions from their normal lattice sites, repulsive interaction parameters determined from perfect crystal data such as the cohesive energy and its spatial derivatives at a single interionic distance should not be expected to be as reliable as parameters obtained from a theoretical calculation of the interaction energy over a range of internuclear distances including those for relaxed positions of the ions.

In Table III are presented LiH crystal parameters calculated by other investigators. Lundquist[4] found upper and lower limits of 8.45 and 8.77 eV/pair for the cohesive energy of LiH by applying the molecular orbital method to the entire crystal with screened hydrogenic wave functions for the H^- and Li^+ ions. For the same wave function in the pairwise interaction model, the cohesive energy is 8.39 eV/pair (Table I). Lowdin[20] has pointed out the importance of three body forces in ionic crystal calculations. Neglect of the forces in this present calculation could account for the difference in energy.

In the diatomic calculation, the large value of the H^- screening parameter required for best fit to crystal data (0.90 as compared with 0.6875 for the free ion) corresponds to the redistribution of the charge of this ion that would arise from a properly symmetrized wave

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[17] O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).

[18] D. R. Stepjens and E. M. Lilley, J. Appl. Phys. **39**, 177 (1967); R. Weil and A. W. Lawson, J. Chem. Phys. **37**, 2730 (1962); F. E. Voronov, V. A. Goncharova, O. V. Stal'gorova, and T. A. Anipova, Fiz. Tverd. Tela **8**, 1643 (1966) [English transl.: Soviet Phys.—Solid State **8**, 1313 (1966)].

[19] Y. Varshni and R. Shukla, Rev. Mod. Phys. **35**, 130 (1963).

[20] P. O. Lowdin, Phil. Mag. Suppl. **5**, 1 (1956).

function,[21] and also takes into account the contraction of the H$^-$ ion in the crystal field.[5] The first of these effects is included in Lundquist's calculation which could account for the much smaller change in screening constant (0.6875–0.7208) required in his case to obtain the best fit to data.

The open-shell function, the only one of the functions considered here which includes enough intrashell correlation energy to yield a bound state for the free H$^-$ ion, leads to a charge distribution for the crystalline H$^-$ which differs markedly from the distribution obtained from the screened hydrogenic function with $\delta_H=0.75$, yet the repulsive interactions obtained for the two cases are almost identical. This result suggests that the finer details of ionic charge distributions may not be very important when repulsive interactions are being calculated, and screened hydrogenic functions may yield adequately detailed charge distributions for this purpose. This type of result has been obtained previously, for example, when Thomas-Fermi type of charge distributions yield interactions almost identical to those found from single or even multiconfiguration MO-SCF calculations.[22] The cohesive energy obtained from Hurst's open shell crystalline H$^-$ function by the diatomic calculation differs from Hurst's result using the same wave function by almost 20%. This difference may be due to the fact that Hurst's calculation was carried out at the experimental interionic distance rather than at the equilibrium value implied by his model or to his neglect of antisymmetrization effects while the diatomic calculation includes them partially.

Finally, the free-ion Hartree-Fock function for H$^-$ leads to a charge distribution which is much too extended to yield a reasonable model for LiH according to the methods used here.

III. SEMICLASSICAL INTERACTIONS

Wedepohl[13] developed a semiclassical interaction method to determine the interactions between like atoms and like ions. The method is generalized here to include the interactions between unlike ions and atoms as well as between like atoms and ions.

A. Model

Atom or ion A (B) has a nuclear charge of Z_ae (Z_be) surrounded by a spherically symmetric electron charge distribution $\rho_a(r_a)$ $[\rho_b(r_b)]$ which contains Q_A (Q_B) electrons. The electron distribution has a finite radius a (b). As a convention it is assumed

$$b\geqslant a. \qquad (7)$$

When the atoms interact it is assumed that the electron distributions do not distort and that each nucleus remains at the center of its electron distribution.

TABLE III. LiH crystal parameters from other investigations.[a]

Investigator	Cohesive energy (eV/pair)	Interionic distance (Å)
I Hylleraas[b]	−9.57	2.21
II Lundquist[c]	−8.70	2.05
III Morita and Takahashi[d]	−9.83	Not calculated
IV Hurst closed shell[e]	−8.74	Not calculated
V Hurst open shell (crystal parameters)	−10.32	Not calculated

[a] Cases III–V have cohesive energies calculated at the experimentally determined lattice distance which is not necessarily where the minimum in the binding energy versus interionic distance curve occurs.

[b] Reference 3.

[c] See Ref. 4. The free ion values are used since the lattice parameter was obtained only for this case.

[d] A. Morita and K. Takahashi, Progr. Theoret. Phys. (Kyoto) **19**, 257 (1958).

[e] See Ref. 5. Closed-shell screened hydrogenic functions with $\delta_H=0.77242$. Open-shell parameters are given elsewhere.

B. Terms in Total Interaction Energy

The total interaction energy is written as

$$E=E_{n_an_b}+E_{e_ae_b}+E_{n_ae_b}+E_{n_be_a}+E_{\mathrm{k}}+E_{\mathrm{ex}}. \qquad (8)$$

The terms on the right-hand side are the electrostatic interaction between the two nuclei, between the two electron distributions, between nucleus A and electrons on B and vice versa, the increase in kinetic energy due to overlap, and the exchange energy. Rationalized mks units are used.

C. Calculation of Electron-Electron Energy

Two elementary charged spherical shells with uniformly distributed charges dq, dq' and having radii x and x' exert a force on each other that depends on the distance r between the centers:

$$\begin{aligned} r>|a+b|, &\quad dF_{ee}=dqdq'/4\pi\epsilon_0r^2, \\ |a+b|<r<|a-b|, &\quad dF_{ee}=(dqdq'/16\pi\epsilon_0r^2) \\ &\qquad\times[2+r^2/xx'-x'/x-x/x'], \\ r<|a-b|, &\quad dF_{ee}=0. \end{aligned}$$

By using these formulas the force between the two spherically symmetric charge distributions can be calculated by integrating between the appropriate limits. There are five cases to consider:

i. No overlap $r>a+b$

$$F_{ee}=Q_AQ_B/4\pi\epsilon_0r^2. \qquad (9)$$

ii. For $b<r<(a+b)$,

$$F_{ee}=\frac{e^2}{4\pi\epsilon_0r^2}\left\{Q_{SA}Q_B+Q_{SB}Q_A-Q_{SA}Q_{SB}+\int_{r-a}^{b}g(y)dy\times\left[\int_{r-b}^{r-y}f(x)dx+\int_{r-y}^{a}\phi(x,y)f(x)dx\right]\right\}, \qquad (10)$$

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[21] A. Westin, I. Waller, and S. O. Lundquist, Arkiv Fysik **22**, 371 (1962).

[22] A. A. Abrahamson (private communication).

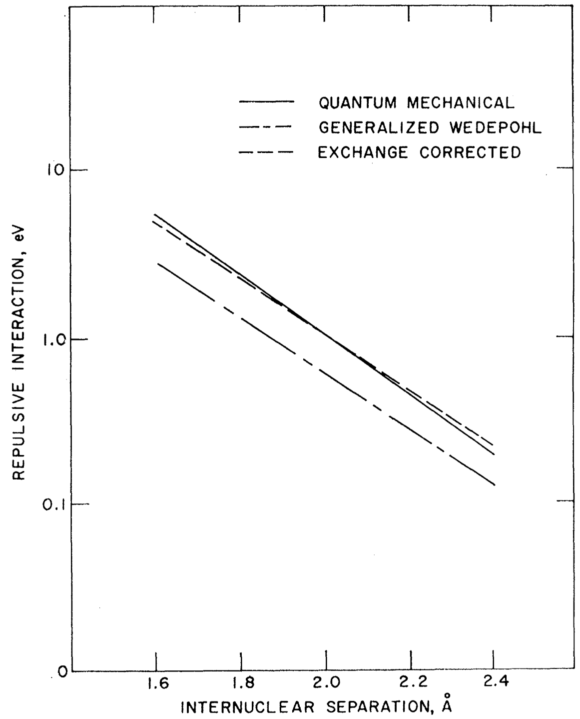

FIG. 3. Semilog plot of Li^+-H^- interactions obtained from screened hydrogenic functions with $\delta_H = 0.95$ by semiclassical and quantum-mechanical calculations.

where

$$f(x) \equiv 4\pi x^2 \rho_a(x), \quad g(y) \equiv 4\pi y^2 \rho_b(y) \tag{11}$$

and

$$\phi(x,y) \equiv \tfrac{1}{4}(2 + r^2/xy - y/x - x/y). \tag{12}$$

Q_{SA} is the total electron charge of atom A in a sphere of radius $r-b$ about nucleus A and Q_{SB} is the total electron charge of atom B in a sphere of radius $r-a$ about nucleus B, i.e.,

$$Q_{SA} \equiv \int_0^{r-b} f(x)dx, \tag{13}$$

$$Q_{SB} \equiv \int_0^{r-a} g(y)dy. \tag{14}$$

iii. The $a<r<b$ case does not occur for identical ions,

$$F_{ee} = e^2/4\pi\epsilon_0 r^2 \left\{ Q_{SB}Q_A + \int_{r-a}^{r} g(y)dy \times \left[\int_0^{r-y} f(x)dx + \int_{r-y}^{a} f(x)\phi(x,y)dx \right] + \int_r^b g(y)dy \int_{y-r}^{a} f(x)\phi(x,y)dx \right\}. \tag{15}$$

If the smaller sphere is inside the larger one, i.e., $r < |a-b|$, then the limits of the last integral over dy change from r to b to r to $(r+a)$.

iv. For $\frac{1}{2}a < r < a$,

$$F_{ee} = e^2/4\pi\epsilon_0 r^2 \left[\int_0^{r} g(y)dy \int_0^{r-y} f(x)dx + \int_0^{r-a} g(y)dy \int_{r-y}^{r+y} \phi(x,y)f(x)dx + \int_{r-a}^{r} g(y)dy \int_{r-y}^{a} f(x)\phi(x,y)dx + \int_r^b g(y)dy \int_{y-r}^{a} f(x)\phi(x,y)dx \right]. \tag{16}$$

If the smaller sphere is inside the larger one then the limits of the last integral over dy change from r to b to r to $(r+a)$.

v. For $r < \frac{1}{2}a$,

$$F_{ee} = e^2/4\pi\epsilon_0 r^2 \left[\int_0^{r} g(y)dy \int_0^{r-y} f(x)dx + \int_0^{r} g(y)dy \int_{r-y}^{r+y} f(x)\phi(x,y)dx + \int_r^{a-r} g(y)dy \int_{y-r}^{y+r} f(x)\phi(x,y)dx + \int_{a-r}^{b} g(y)dy \int_{y-r}^{a} f(x)\phi(x,y)dx \right]. \tag{17}$$

If the smaller sphere is inside the larger the limits on the last integral over dy change from $(a-r)$ to b to $(a-r)$ to $(r+a)$.

The electron-electron interaction energy is determined by integrating the force from the internuclear separation r to infinity,

$$E_{ee} = Q_A Q_B e^2/4\pi\epsilon_0(a+b) + \int_r^{a+b} F_{ee}(r')dr'. \tag{18}$$

The first term is just the value of the integral of the force from $(a+b)$ to infinity.

D. Electron Nuclear Interactions

The interaction between the electrons of one ion and the nucleus of the other ion is calculated from elementary electrostatics. The interaction between the electrons of A and the nucleus of B is

$$E_{n_b e_a} = -Q_A Z_b e^2/4\pi\epsilon_0 r\,, \quad r>a$$

$$E_{n_a e_b} = -\frac{Z_b e^2}{4\pi\epsilon_0}\left\{\frac{Q_A}{a} + \int_r^a \frac{1}{r'^2} \times\left[\int_0^{r'} 4\pi y^2 \rho_a(y)dy\right]dr'\right\}\,, \quad r<a. \qquad (19)$$

E. Calculation of Kinetic and Exchange Energies

The increase in the kinetic energy due to overlap is given as

$$E_k = K_k \int \{[\rho_a(r)+\rho_b(r)]^{5/3} - \rho_a(r)^{5/3} - \rho_b(r)^{5/3}\} d\tau \qquad (20)$$

with

$$K_k = \tfrac{3}{5}(h^2\pi^2/2m)(3/\pi)^{2/3}. \qquad (21)$$

The integration is over the overlap region. The exchange integral is evaluated using the Thomas-Fermi-Dirac equation for exchange. In (20) the 5/3 powers are replaced by 4/3 powers and K_k is replaced by

$$K = (3/16\pi\epsilon_0)(3/\pi)^{1/3}e^2. \qquad (22)$$

F. Discussion

The equations were programmed for the Brookhaven CDC 6600 computer. Using the same screened hydrogenic charge distributions for the Li^+ and H^- used in Sec. II, semiclassical interactions were obtained for the same systems. The radii of the charge distributions were increased until the values did not affect the interactions to the accuracy desired. For the various screening parameters considered, the Li^+-H^- semiclassical interactions were also well represented by Born-Mayer forms. The results had an exponential dependence in reasonable agreement with the diatomic quantum-mechanical interactions, but the values of the interactions are about 40% too low. Similar results were found when the semiclassical interactions for H^--H^- are compared with the diatomic quantum-mechanical results. A typical set of results is shown in Fig. 3 for the Li^+-H^- interaction with a H screening parameter of 0.9.

To improve the method a more extensive treatment of exchange effects was attempted. The exchange energy is a correction to the electron-electron repulsion term to account for the correlation in motion of electrons with the same spin. The effect of the redistribution of the electron distributions due to overlap on the electron-nuclear interactions is considered.

A specific system, Li^+-H^-, is considered, but the results are quite general. If $a(r_a)$ and $b(r_b)$ are the one-electron wave functions about the Li^+ and H^-, respectively, then we can account for exchange effects in LiH by writing the wave function as a four by four determinant. The resulting charge distribution taking exchange effects into account is

$$\rho(r) = -(1+s^2)2a^2(r) - (1+s^2)2b^2(r) + 4sa(r)b(r)\,, \qquad (23)$$

where s is the overlap integral

$$s \equiv \langle a|b\rangle. \qquad (24)$$

The charge distribution may be considered as being made up of a negative "electronic" charge distribution, ρ_{el},

$$\rho_{\mathrm{el}}(r) = -(1+s^2)[2a^2(r)+2b^2(r)]\,,$$

which is the superposition of the free-ion charge distributions increased by a factor $(1+s^2)$, and an "exchange" charge distribution, ρ_{ex},

$$\rho_{\mathrm{ex}}(r) = +4sa(r)b(r)\,,$$

which is a positive charge distribution concentrated in the region between the ions. The exchange energy is physically equivalent to the interactions between the exchange charge and the electron distributions. Dick and Overhauser[23] first proposed representing this exchange charge as a point charge of magnitude $+4s^2$ lying on the internuclear axis between the ions. This approximation for representing exchange effects has also been applied to ionic systems by Hafemeister and Zahrt.[6] Following the procedure used by the above authors, the effects of exchange on the electron-nuclear interaction can be accounted for by considering the interaction between the exchange charge and the nuclei. Since the exchange charge and the nuclei have the same sign of charge, this energy will be positive and will increase the interaction energy. In Fig. 3 the effect of adding this exchange correction is demonstrated, and it is shown to bring the semiclassical interactions into reasonable agreement with the diatomic quantum-mechanical calculations when the same screened hydrogenic functions with $\delta_H = 0.95$ are used for both calculations.

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It is a pleasure to thank Dr. G. J. Dienes for his constant interest in this work and for providing many useful ideas. One of us (C.R.F.) would also like to thank Dr. R. E. Watson for his interest and suggestions.

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[23] B. G. Dick and A. Overhauser, Phys. Rev. **112**, 90 (1958).