

Simple Calculation of the Lattice Energy of Lithium Hydride

Undergraduate chemistry majors, by the time they graduate, have generally been introduced to the quantum mechanical treatments of the H atom, the He atom, the H_2^+ molecule ion and the H_2 molecule. From a study of these simple systems we hope that our students become familiar with the postulates of quantum theory and the quantum mechanical explanation of atomic and molecular structure and stability. Recognizing the usefulness of the study of simple systems as an aid to learning, this paper presents a quantum mechanical model of the simple ionic solid—LiH(s).

The Model

Lithium hydride is a white crystalline solid with the face-centered cubic crystal structure. The model for LiH(s) proposed in this study consists of the following assumptions

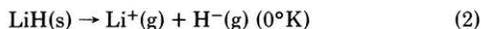
- 1) The bonding in LiH(s) is completely ionic. That is, the lattice sites are occupied by the spherical, two electron ions, Li^+ and H^- .
- 2) The electrons of Li^+ and H^- occupy hydrogen-like 1s orbitals with a scale-factor, Z , introduced so that the size of the ions may be varied. Expressed in atomic units, the electronic wavefunctions for Li^+ and H^- have the form¹

$$\Psi(1,2) = 1s(1)1s(2) = (Z^3/\pi) \exp[-Z(r_1 + r_2)] \quad (1)$$

The scale factor, as it appears in the above wavefunction, determines how rapidly the wavefunction (and, therefore, the electron density) diminishes as the distance from the nucleus increases. Z is thus simply related to the radius of the ion: the larger the value of Z the more rapidly the electron density diminishes and, therefore, the smaller the ionic radius.

- 3) Since the average value of the distance of an electron from the nucleus, $\langle r \rangle$, in a 1s orbital is $1.5/Z$, it seems reasonable to take $2\langle r \rangle$ or $3/Z$ as the effective ionic radius in the solid. It is easy to show that 94% of the charge is contained within this radius.
- 4) Van der Waals interactions between the electron clouds of the ions and the quantum mechanical zero-point energy of the lattice are neglected.

To check the validity of this model the lattice energy of LiH(s) is calculated and compared with the value obtained from a Born-Haber analysis. The lattice energy is defined as the energy required to bring about the following process



The determination of the lattice energy on the basis of the proposed model, therefore, proceeds by calculating the ground-state energies of $Li^+(g)$ and $H^-(g)$ and subtracting from them the ground-state energy calculated for LiH(s). Since terms for the kinetic energy of the nuclei are not included, the calculations refer to $0^\circ K$.

$Li^+(g)$ and $H^-(g)$

The calculations for the ground-state energies of $Li^+(g)$ and $H^-(g)$ are similar to that of He. The energy operators consist of five terms: kinetic energy operators for each of the electrons, electron-nuclear potential energy operators for each of the electrons and an electron-electron potential energy operator.¹

$$\hat{H}_{Li^+} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 3/r_1 - 3/r_2 + 1/r_{12} \quad (3)$$

$$\hat{H}_{H^-} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + 1/r_{12} \quad (4)$$

The energy operators are expressed in atomic units. In eqns. (3) and (4), r_1 is the distance of electron 1 from the nucleus,

Table 1. Ground State Energies for $Li^+(g)$ and $H^-(g)$ in a.u.

Ion	$\langle E \rangle$	$\langle T \rangle$	$\langle V \rangle$	Z^a
$Li^+(g)$	-7.22	7.22	-14.44	2.69 (0.59 Å)
$H^-(g)$	-0.47	0.47	-0.95	0.69 (2.30 Å)

^a The quantities in parentheses are the gas-phase ionic radii as calculated by the criterion proposed in assumption 3 in the text: $R = (3/Z \text{ a.u.}) (0.529 \text{ Å/a.u.})$.

r_2 is the distance of electron 2 from the nucleus, and r_{12} is the electron-electron distance.

The trial wavefunction and the appropriate energy operator are substituted into the following equation

$$E = \int \Psi(1,2) \hat{H} \Psi(1,2) d\tau_1 d\tau_2 \quad (5)$$

Calculation of the ground-state energy using eqn. (5) yields the usual integrals, which are discussed briefly in the appendix. When the integrals are evaluated the following expressions result¹

$$E_{Li^+} = Z_+^2 - 6Z_+ + 0.625Z_+ \quad (6)$$

$$E_{H^-} = Z_-^2 - 2Z_- + 0.625Z_- \quad (7)$$

These expressions are minimized with respect to the parameters Z_+ and Z_- , the scale factors for the cation and anion, respectively. The results are summarized in Table 1.

LiH(s)

The ground-state energy of LiH(s) consists of three terms: the internal energy of Li^+ , the internal energy of H^- , and the coulombic interaction energy of the ions occupying the lattice sites.

$$E_{LiH} = E_{Li^+} + E_{H^-} + E_{coul} \quad (8)$$

From the results of the previous section and the knowledge that lithium hydride has the face-centered crystal structure, eqn. (8) can be written

$$E_{LiH} = Z_+'^2 - 5.375Z_+' + Z_-'^2 Z - 1.3752Z_-' + E_{coul} \quad (9)$$

where

$$E_{coul} = -1.748/(R_+ + R_-); \text{ for } R_+/R_- \geq .414$$

$$E_{coul} = -1.748/(\sqrt{2}R_-); \text{ for } R_+/R_- < .414$$

Here 1.748 is the Madelung constant for the face-centered cubic structure for singly charged ions. R_+ and R_- are the radii of the cation and anion. $(R_+ + R_-)$ is the inter-ionic distance for situations $(R_+/R_- \geq 0.414)$ in which the cations and anions "touch." $\sqrt{2}R_-$ is the inter-ionic distance for those circumstances $(R_+/R_- < 0.414)$ in which the cation "rattles" in the octahedral hole created by the anions. Z_+' and Z_-' are the scale factors for the ions in the solid state. Since the size of the ions may change on the formation of the solid, they are not necessarily equal to the gas-phase scale factors, Z_+ and Z_- .

On the basis of assumption 3, R_+ and R_- are replaced by $3Z_+'$ and $3/Z_-'$, the effective ionic radii of the cation and anion. The coulombic contribution to eqn. (9) now has the form

¹ Linnett, J. W., "Wave Mechanics and Valency," Barnes and Noble, New York, 1966, pp. 61-66.

² Pauling, L., and Wilson, E. B., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., New York, 1935, p. 446.

Table 2. Summary of the LiH(s) Calculation

Cation scale factor, Z'_+	2.69
Anion scale factor, Z'_-	0.89
Cation radius, R_+	0.59 Å (0.60 Å) ^a
Anion radius, R_-	1.78 Å (2.08 Å) ^a
Ground-state energy, E_{LiH}	-8.02 a.u.

^aPauling, L., "The Nature of the Chemical Bond," 3rd Ed., Ithaca, New York, Cornell University Press, 1960.

Table 3. Born-Haber Calculation of Lattice Energy for LiH(s)^a

$\text{Li}^+(\text{g}) + \text{H}^-(\text{g})$		
196.3 Kcal/mole	↑	$I.P. = 124.3$ Kcal/mole $E.A. = -17.2$ Kcal/mole
	↑	$\text{Li}(\text{g}) + \text{H}(\text{g})$
89.2 Kcal/mole	↑	$\Delta H_{\text{sub}} = 37.1$ Kcal/mole $\frac{1}{2} D_0 = 52.1$ Kcal/mole
	↑	$\text{Li}(\text{s}) + \frac{1}{2} \text{H}_2(\text{g})$
0		
	↓	$\Delta H_{\text{form}} = -21.6$ Kcal/mole
-21.6 Kcal/mole	↓	$\text{LiH}(\text{s})$
	↑	$U_{\text{LiH}} = 217.9$ Kcal/mole

^aAll thermochemical data taken from 56th edition of the "Handbook of Chemistry and Physics."

$$E_{\text{coul}} = -1.748/(3/Z'_+ + 3/Z'_-); \text{ for } Z'_-/Z'_+ \geq .414 \quad (10)$$

$$E_{\text{coul}} = -1.748/(\sqrt{2}(3/Z'_-)); \text{ for } Z'_-/Z'_+ < .414$$

Substituting eqn. (10) into eqn. (9) and varying Z'_+ and Z'_- until a minimum is found, yields the ground-state energy of LiH(s). The results of this minimization process are summarized in Table 2.

Lattice Energy

The calculated lattice energy for LiH(s) is

$$\begin{aligned} U &= E_{\text{Li}^+} + E_{\text{H}^-} - E_{\text{LiH}} \\ &= (-7.22 \text{ a.u.} - 0.47 \text{ a.u.}) + 8.02 \text{ a.u.} \\ &= 0.33 \text{ a.u.} = 207 \text{ Kcal/mole} \end{aligned}$$

This value is within 5% of the Born-Haber value of 217.9 Kcal/mole calculated in Table 3. The calculated values for the ionic radii are also in reasonable agreement with experimental values as is indicated in Table 2.

In addition the model provides a clear picture of the stability of ionic solids. Equation 9 contains four types of energy terms: electron kinetic energy, T ; electron-nuclear potential energy, V_{EN} ; intra-ion, electron-electron potential energy, V_{EE} ; and coulombic energy (inter-ion potential energy), E_{coul} . V_{EN} and E_{coul} are negative and favored by small ionic radii (large scale factors). The V_{EE} and T contributions are positive and favored by large ionic radii (small scale factors). The stability of the lattice, then, is due to a balance between these two types of energy terms. The lattice does not collapse under the influence of the "attractive" terms, V_{EN} and E_{coul} , because of the "repulsive" character of V_{EE} and T . Since the kinetic energy terms are proportional to the scale factor squared, and, therefore, inversely proportional to the square of the ionic radii, they become very large as the ionic radii decrease. It is

this large increase in the electron kinetic energy which is mainly responsible for the "repulsive forces" which prevent the collapse of the lattice.

In addition to providing a succinct picture of ionic stability, this model has the advantage that its only parameters, the scale factors for the cation and anion (Z_+ and Z_-), have immediate physical significance. They are simply related to the radii of the ions, Li^+ and H^- . This type of conceptual simplicity can be of great value to undergraduates.

Appendix

The case of the lithium ion will be used as an example of how eqns. (6) and (7) are obtained. When the trial wavefunction of eqn. (1) and the $\text{Li}^+(\text{g})$ energy operator, eqn. (3), are substituted into eqn. (5), five integrals result: kinetic energy integrals for each of the electrons, electron-nuclear potential energy integrals for each of the electrons, and an electron-electron potential energy integral

$$\begin{aligned} E_{\text{Li}^+} &= \langle 1s^*(1) | -\frac{1}{2}\nabla_1^2 | 1s(1) \rangle + \langle 1s^*(2) | -\frac{1}{2}\nabla_2^2 | 1s(2) \rangle + \\ &\quad \langle 1s^*(1) | -3/r_1 | 1s(1) \rangle + \langle 1s^*(2) | -3/r_2 | 1s(2) \rangle + \\ &\quad \langle 1s^*(1)1s^*(2) | 1/r_{12} | 1s(1)1s(2) \rangle \quad (11) \end{aligned}$$

The kinetic energy of a hydrogen 1s electron is 0.5 a.u. The trial wavefunctions used here differ from the hydrogen 1s functions only by the scale factor Z . It is not difficult to show that the kinetic energy integrals above are each equal to $0.5 Z_+^2$ a.u., giving a total kinetic energy of Z_+^2 . The potential energy of a hydrogen 1s electron is -1.0 a.u. Because of the scale factor and the +3 charge on the lithium nucleus, the electron-nuclear potential energy integrals in eqn. (11) are each equal to $-3.0 Z_+$ a.u., giving a total electron-nuclear potential energy of $-6 Z_+$.

Because of the spherical symmetry of the $1s^2$ electron configuration the electron-electron potential energy integral is equivalent to

$$\int_0^\infty \varphi_1(r_2) 1s(r_2)^2 4\pi r_2^2 dr_2 \quad (12)$$

where $\varphi_1(r_2)$ is the electronic potential of electron 1 at r_2 , the coordinate of electron 2. The electron-electron potential energy can be interpreted as the average value of the potential energy of electron 2 in the electrostatic field created by electron 1.

The electric potential due to a spherical charge distribution at some distance r_2 from the center of the charge distribution is a sum of two contributions

$$\begin{aligned} \varphi_1(r_2) &= (1/r_2) \int_0^{r_2} 1s(r_1)^2 4\pi r_1^2 dr_1 + \\ &\quad \int_{r_2}^\infty \frac{1s(r_1)^2 4\pi r_1^2 dr_1}{r_1} \quad (13) \end{aligned}$$

Relative to position r_2 , all the electron density with $r < r_2$ behaves as if it were a point charge located at the origin. This contribution is the first term on the right side of eqn. (13). Relative to r_2 , the charge lying beyond r_2 can be thought of as consisting of very many, very thin shells of thickness dr_1 , of volume $4\pi r_1^2 dr_1$ and containing charge $1s(r_1)^2 4\pi r_1^2 dr_1$. The potential due to a spherical shell, anywhere inside the shell, is the same as it is at the center of the shell. Therefore, the potential at r_2 due to the charge lying beyond r_2 is the sum of the contributions from all the shells lying beyond r_2 and is given by the second term in eqn. (13).

Evaluating the integrals on the right side of eqn. (13) yields

$$\varphi_1(r_2) = (1/r_2)[1 - \exp(-2Z_+r_2)] - Z_+ \exp(-2Z_+r_2) \quad (14)$$

When eqn. (14) is substituted into eqn. (12) and the integral evaluated, the result is $0.625 Z_+$.