

A Lattice Energy Calculation for LiH

Frank Rioux

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

1. The bonding in LiH(s) is completely ionic. The lattice sites are occupied by the spherical, two-electron ions, Li^+ and H^- .

2. The electrons of Li^+ and H^- occupy hydrogenic 1s atomic orbitals with adjustable scale factors α and β , respectively. Expressed in atomic units the wavefunctions have the form,

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

The scale factor determines how rapidly the wavefunction (and, therefore, the electron density) diminishes as the distance from the nucleus increases. α and β are, therefore, inversely related to the atomic radius. The larger α and β , the smaller the ionic radii are.

3. The average distance of an electron from the nucleus, $\langle r \rangle$, in a scaled 1s orbital is $1.5/\alpha$. Therefore, it seems reasonable to take $2\langle r \rangle$, or $3/\alpha$ as the effective ionic radius in the solid. It is easy to show that 94% of the charge is contained within this radius. (See Appendix)

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) will be calculated and compared to the value obtained by 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 $\text{Li}^+(\text{g})$ and $\text{H}^-(\text{g})$, and subtracting from them the ground state energy of LiH(s). Since terms for the kinetic energy of the ions are not included, the calculations refer to absolute zero.

$\text{Li}^+(\text{g})$ and $\text{H}^-(\text{g})$

The calculations for the ground-state energies of $\text{Li}^+(\text{g})$ and $\text{H}^-(\text{g})$ 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.

$$H_{\text{Li}} = -\frac{1}{2 \cdot r_1} \cdot \frac{d^2}{dr_1^2} r_1 - \frac{1}{2 \cdot r_2} \cdot \frac{d^2}{dr_2^2} r_2 - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}}$$

$$H_{\text{H}} = -\frac{1}{2 \cdot r_1} \cdot \frac{d^2}{dr_1^2} r_1 - \frac{1}{2 \cdot r_2} \cdot \frac{d^2}{dr_2^2} r_2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

When the trial wavefunction and the appropriate energy operator is used in the variational integral,

$$E = \int_0^\infty \Psi(1,2) \cdot H \cdot \Psi(1,2) d\tau_1 \cdot d\tau_2$$

the following expressions result (see Appendix for details): $E_{\text{Li}} = \alpha^2 - 6 \cdot \alpha + \frac{5}{8} \cdot \alpha$ $E_{\text{H}} = \beta^2 - 2 \cdot \beta + \frac{5}{8} \cdot \beta$

Minimization of the energy with respect to the scale factors to obtain the ground state energies of the gas-phase ions is the next step.

Calculation of the energies of the gas phase ions:

Seed value for the cation scale factor: $\alpha := 3$

Calculate the energy and radius of the gas phase cation: $E_{\text{Li}}(\alpha) := \alpha^2 - 5.375 \cdot \alpha$

$\alpha := \text{Minimize}(E_{\text{Li}}, \alpha)$ $\alpha = 2.6875$ $E_{\text{Li}}(\alpha) = -7.2227$ $E_{\text{Li}} := E_{\text{Li}}(\alpha)$ $R_{\text{Li}} := \frac{3}{\alpha}$ $R_{\text{Li}} = 1.1163$

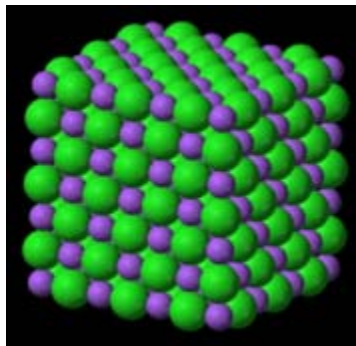
Seed value for the anion scale factor: $\beta := 1$

Calculate the energy and radius of the gas phase anion: $E_{\text{H}}(\beta) := \beta^2 - 1.375 \cdot \beta$

$\beta := \text{Minimize}(E_{\text{H}}, \beta)$ $\beta = 0.6875$ $E_{\text{H}}(\beta) = -0.4727$ $E_{\text{H}} := E_{\text{H}}(\beta)$ $R_{\text{H}} := \frac{3}{\beta}$ $R_{\text{H}} = 4.3636$

Lithium hydride solid - LiH(s)

As noted above, LiH has the face-centered cubic structure shown below.



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.

$$E_{\text{LiH}} = E_{\text{Li}} + E_{\text{H}} + E_{\text{coul}}$$

From the results of the previous section and the knowledge that lithium hydride has the face-centered crystal structure, this equation can be written

$$E_{\text{LiH}} = \alpha^2 - 5.375 \cdot \alpha + \beta^2 - 1.375 \cdot \beta + E_{\text{coul}}$$

where

$$E_{\text{coul}} = -\frac{1.748}{R_{\text{c}} + R_{\text{a}}} \quad \text{for } R_{\text{c}}/R_{\text{a}} \geq .414 \quad E_{\text{coul}} = -\frac{1.748}{\sqrt{2} \cdot R_{\text{a}}} \quad \text{for } R_{\text{c}}/R_{\text{a}} < .414$$

Here 1.748 is the Madelung constant for the face-centered cubic structure for singly charged ions. R_c and R_a are the radii of the cation and anion. $(R_c + R_a)$ is the inter-ionic separation for situations ($R_c/R_a \geq .414$) in which there is cation-anion contact, while $1.414R_a$ is the inter-ionic separation for those circumstances ($R_c/R_a < .414$) in which there is only anion-anion contact. On the basis of assumption 3 of the model, R_c and R_a are replaced by $3/\alpha$ and $3/\beta$, the effective ionic radii of the cation and the anion. The coulombic contribution now has the form

$$E_{\text{coul}} = -\frac{1.748}{\frac{3}{\alpha} + \frac{3}{\beta}} \quad \text{for } \beta/\alpha \geq .414 \quad E_{\text{coul}} = -\frac{1.748}{\frac{\sqrt{2} \cdot 3}{\beta}} \quad \text{for } \beta/\alpha < .414$$

Minimization of the energy of the solid simultaneously with respect to α and β is outlined below.

Energy of the solid assuming anion-cation contact. $f(\alpha, \beta) := \alpha^2 - 5.375 \cdot \alpha + \beta^2 - 1.375 \cdot \beta - \frac{1.748}{\frac{3}{\alpha} + \frac{3}{\beta}}$

Energy of the solid assuming anion-anion contact and that the cation rattles in the octahedral hole. $g(\alpha, \beta) := \alpha^2 - 5.375 \cdot \alpha + \beta^2 - 1.375 \cdot \beta - \frac{1.748 \cdot \beta}{3 \cdot \sqrt{2}}$

Composite expression for the energy of the solid using a conditional statement $E_{\text{LiH}}(\alpha, \beta) := \text{if}\left(\frac{\beta}{\alpha} \geq .414, f(\alpha, \beta), g(\alpha, \beta)\right)$

Minimization of the energy of LiH with respect to the parameters α and β .

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} := \text{Minimize}(E_{\text{LiH}}, \alpha, \beta)$$

$$\alpha = 2.6875 \quad R_c := \frac{3}{\alpha} \quad R_c = 1.1163 \quad R_c (\text{experimental}) = 1.134$$

$$\beta = 0.8935 \quad R_a := \frac{3}{\beta} \quad R_a = 3.3576 \quad R_a (\text{experimental}) = 3.931$$

$$E_{\text{LiH}}(\alpha, \beta) = -8.0210 \quad E_{\text{LiH}} := E_{\text{LiH}}(\alpha, \beta)$$

Comparison of gas-phase and solid-state ion energies (see Appendix for interpretation):

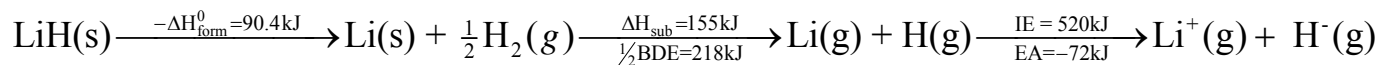
Cation: $E_{\text{Lis}} := \alpha^2 - 5.375 \cdot \alpha \quad E_{\text{Lis}} = -7.2227 \quad E_{\text{Li}} = -7.2227 \quad \text{Cation energy doesn't change.}$

Anion: $E_{\text{Hs}} := \beta^2 - 1.375 \cdot \beta \quad E_{\text{Hs}} = -0.4302 \quad E_{\text{H}} = -0.4727 \quad \text{Anion energy increases.}$

Coulomb energy in solid state: $E_{\text{LiH}} - E_{\text{Lis}} - E_{\text{Hs}} = -0.3681$

The calculated lattice energy for LiH(s): $U_{\text{Lattice}} := E_{\text{Li}} + E_{\text{H}} - E_{\text{LiH}} \quad U_{\text{Lattice}} = 0.3257$

This result in atomic units is equivalent to a lattice energy expressed in SI units of 856 kJ/mol. A Born-Haber analysis (see below) yields a lattice energy of 912 kJ/mol. Thus, the calculated result of the proposed model is in error by only 6%. The errors for the solid-state ionic radii are 1.6% (cation) and 14.6% (anion). Given the simplicity of the model these comparisons with experimental data are encouraging. For further details on this model see the reference cited below.



F. Rioux, "Simple Calculation of the Lattice Energy of Lithium Hydride," *Journal of Chemical Education* **54**, 555 (1977).

Appendix:

$$\int_0^{\frac{3}{\alpha}} \left(\sqrt{\frac{\alpha^3}{\pi}} \cdot \exp(-\alpha \cdot r) \right)^2 \cdot 4 \cdot \pi \cdot r^2 \, dr = 93.8 \%$$

The table below provides a summary of the lattice energy calculation carried out in this tutorial.

Property	GasPhase	SolidState
Cation, α	2.6875	2.6875
CationRadius	1.1163	1.163
CationEnergy	-7.2227	-7.2227
Anion, β	0.6875	0.8935
AnionRadius	4.364	3.3576
AnionEnergy	-0.4727	-0.4302
InterIon		
CoulombEnergy	x	-0.3681
TotalEnergy	-7.6953	-8.0210
LatticeEnergy	x	0.3257

From the table it is clear that in the formation of LiH solid, the hydride anion contracts significantly from its gas-phase size. This increases its energy ($-0.4302 + 0.4727 = 0.0425$). The increase in anion energy is more than offset by the attractive inter-ion coulombic energy (-0.3681). In other words, the anion suffers a modest increase in energy by shrinking in size so that it can be on-average closer to the cation, thereby increasing the coulombic attraction between the ions and leading to a stable ionic solid.

Most of the integrals required in the analysis above are now evaluated.

Previous memory of α and β values is cleared: $\alpha := \alpha$ $\beta := \beta$

Trial one-electron wavefunction: $\Psi(r, \beta) := \sqrt{\frac{\beta^3}{\pi}} \cdot \exp(-\beta \cdot r)$

Demonstrate that it is normalized: $\int_0^{\infty} \Psi(r, \beta)^2 \cdot 4 \cdot \pi \cdot r^2 dr$ assume, $\beta > 0 \rightarrow 1$

Calculate the average value of the electron's distance from the nucleus: $R(\beta) := \int_0^{\infty} \Psi(r, \beta) \cdot r \cdot \Psi(r, \beta) \cdot 4 \cdot \pi \cdot r^2 dr$ assume, $\beta > 0 \rightarrow \frac{3}{2 \cdot \beta}$

Calculate the average value of the kinetic energy of the electron:

$$T(\beta) := \int_0^{\infty} \Psi(r, \beta) \cdot \left(-\frac{1}{2 \cdot r}\right) \cdot \frac{d^2}{dr^2}(r \cdot \Psi(r, \beta)) \cdot 4 \cdot \pi \cdot r^2 dr \text{ assume, } \beta > 0 \rightarrow \frac{\beta^2}{2}$$

Calculate the average value of the electron-nucleus potential energy:

$$V(\beta, Z) := \int_0^{\infty} \Psi(r, \beta) \cdot \left(-\frac{Z}{r}\right) \cdot \Psi(r, \beta) \cdot 4 \cdot \pi \cdot r^2 dr \text{ assume, } \beta > 0 \rightarrow -Z \cdot \beta$$

Calculate the average value of the electron-electron potential energy in two steps:

1. The electrostatic potential at r due to electron 1 is:

$$\Phi(r, \beta) := \frac{1}{r} \cdot \int_0^r \Psi(x, \beta)^2 \cdot 4 \cdot \pi \cdot x^2 dx + \int_r^{\infty} \frac{\Psi(x, \beta)^2 \cdot 4 \cdot \pi \cdot x^2}{x} dx \quad \left| \begin{array}{l} \text{assume, } \beta > 0 \\ \text{simplify} \end{array} \right. \rightarrow -\frac{e^{-2 \cdot \beta \cdot r} + \beta \cdot r \cdot e^{-2 \cdot \beta \cdot r} - 1}{r}$$

2. The electrostatic interaction between the two electrons is:

$$V_{EE}(\beta) := \int_0^{\infty} \Phi(r, \beta) \cdot \Psi(r, \beta)^2 \cdot 4 \cdot \pi \cdot r^2 dr \quad \left| \begin{array}{l} \text{assume, } \beta > 0 \\ \text{simplify} \end{array} \right. \rightarrow \frac{5 \cdot \beta}{8}$$

To summarize, the trial wavefunction chosen for two electron systems lead to the following expression for the energy.

$$E(Z, \beta) = \beta^2 - 2 \cdot Z \cdot \beta + \frac{5}{8} \cdot \beta = \beta^2 - 2 \cdot \beta \cdot \left(Z - \frac{5}{16}\right)$$

Minimization of the energy with respect to the variational parameter β yields: $\beta = Z - \frac{5}{16}$

Ground state energy: $E(Z) = -\left(Z - \frac{5}{16}\right)^2$ Ionic radius: $R_Z = \frac{3}{Z - \frac{5}{16}}$