

## A Lattice Energy Calculation for LiH

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 elements:

1. The bonding in LiH(s) is completely ionic. The lattice sites are occupied by the spherical, two-electron ions, Li<sup>+</sup> and H<sup>-</sup>, with electronic structure 1s<sup>2</sup>.

2. The electrons of Li<sup>+</sup> and H<sup>-</sup> occupy hydrogenic 1s atomic orbitals with adjustable scale factor  $\alpha$ . 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 and, therefore, is inversely related to the atomic radius. The larger  $\alpha$  the smaller the ionic radius.

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. It is easy to show that 94% of the charge is contained within this radius. (See the Appendix for computational details.)

4. It is also assumed that the Li<sup>+</sup> and H<sup>-</sup> ions in the solid have the same  $\alpha$  value, energy and radius as they do in the gas phase. Under this assumption the lattice energy is the negative of the inter-ion coulombic energy in the solid state.

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



### Li<sup>+</sup>(g) and H<sup>-</sup>(g)

We begin with variational calculations for the ground-state energies of Li<sup>+</sup>(g) and H<sup>-</sup>(g). These calculations will yield the ionic radii which will subsequently be used to calculate the LiH lattice energy.

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 the appendix for computational details) :

$$E_{\text{Li}}(\alpha) := \alpha^2 - 6 \cdot \alpha + \frac{5}{8} \cdot \alpha \quad E_{\text{H}}(\alpha) := \alpha^2 - 2 \cdot \alpha + \frac{5}{8} \cdot \alpha$$

Minimization of the energy with respect to the scale factors to obtain the ground state energies and radii of the ions is shown below.

### Calculation of the energies and radii of the gas phase ions:

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

Energy and radius of the gas phase cation:  $\alpha := \text{Minimize}(E_{\text{Li}}, \alpha) \quad \alpha = 2.6875 \quad E_{\text{Li}}(\alpha) = -7.2227$

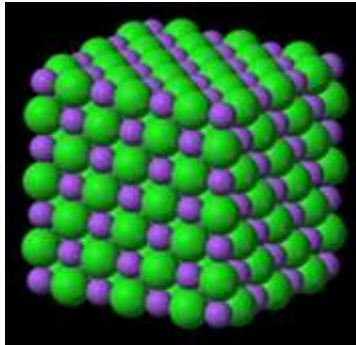
$$R_{\text{Li}} := \frac{3}{\alpha} \quad R_{\text{Li}} = 1.1163$$

Energy and radius of the gas phase anion:  $\alpha := \text{Minimize}(E_{\text{H}}, \alpha) \quad \alpha = 0.6875 \quad E_{\text{H}}(\alpha) = -0.4727$

$$R_{\text{H}} := \frac{3}{\alpha} \quad R_{\text{H}} = 4.3636$$

### 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  $\text{Li}^+$ , the internal energy of  $\text{H}^-$ , and the coulombic interaction energy of the ions occupying the lattice sites.

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

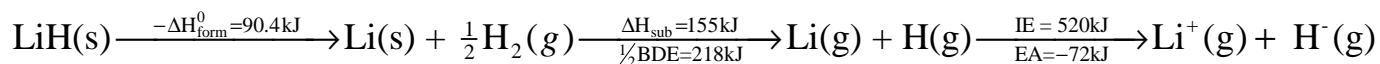
Assuming a face-centered structure (Madelund constant = 1.748) with cation-anion and anion-anion contact, the coulombic term is as shown below.

$$E_{\text{Li}}(2.6875) + E_{\text{H}}(0.6875) - \frac{1.748}{R_{\text{Li}} + R_{\text{H}}} = -8.0143$$

Since it has been assumed that the  $\text{Li}^+(\text{g})$  and  $\text{H}^-(\text{g})$  ions are the same in the gas phase and the solid state, the lattice energy is the negative of  $E_{\text{coul}}$ .

$$U_{\text{Lattice}} := \frac{1.748}{R_{\text{Li}} + R_{\text{H}}} \quad U_{\text{Lattice}} = 0.319$$

This result in atomic units is equivalent to a lattice energy expressed in SI units of 838 kJ/mol. The Born-Haber analysis shown below yields a lattice energy of 912 kJ/mol. Thus, the calculated result of the proposed model is in error by 8%.



Improved results can be obtained by allowing the gas phase ions to change size on the formation of the solid under the influence of the inter-ion coulombic interaction, and by abandoning the simplifying restriction of cation-anion and anion-anion contact. See the reference below for an outline of such a calculation.

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

## Appendix

Because this is a live Mathcad document and the scale factor,  $\alpha$ , has been used above,  $\beta$  will be used for the calculations outlined below.

Trial one-electron wavefunction:

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

Demonstrate that it is normalized:

$$\int_0^{\infty} \Psi(r, \beta)^2 \cdot 4 \cdot \pi \cdot r^2 \, dr \text{ assume, } \beta > 0 \rightarrow 1$$

Calculate the average value of the electron's distance from the nucleus:

$$R(\beta) := \int_0^{\infty} \Psi(r, \beta) \cdot r \cdot \Psi(r, \beta) \cdot 4 \cdot \pi \cdot r^2 \, dr \text{ assume, } \beta > 0 \rightarrow \frac{3}{2 \cdot \beta}$$

Demonstrate 94% of electron density is contained within  $2 \langle r \rangle$ :

$$\int_0^{\frac{3}{\beta}} \Psi(r, \beta)^2 \cdot 4 \cdot \pi \cdot r^2 \, dr \text{ assume, } \beta > 0 \rightarrow (-25) \cdot e^{-6} + 1 = 93.8 \%$$

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

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

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

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

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

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

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

2. The electrostatic interaction between the two electrons is:

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

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  $\beta$  yields:  $\beta = Z - \frac{5}{16}$

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