The pair potential for an ionic bond is to add the attractive Coulomb potential energy to L-J potential, eq.(1) from last class, to get:

\[
V(r) = -\frac{ke^2 Z_1 Z_2}{r} + 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(1)

The total lattice energy is written by modifying eq.(1) to include the Madelung constant (\(\alpha\)), \(n_1\) and \(n_2\) stoichiometry, and the number of nearest neighbor (\(N\)) contributions to L-J portion of the energy [long range attractive contributions can be added but in most cases are negligible for ionic bonding].

New expression for lattice energy \((V)\) as a function of separation \((r)\) for binary crystals is:

\[
V(r) = -\frac{ke^2 \alpha (n_1 + n_2) Z_1 Z_2}{2r} + 4N\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(2)

Since \(\alpha\) varies over a small range, variations in the chemistry of the compound affect total lattice energy more than variations in the structural configuration.

Appropriate pair potentials for ionic materials must contain an electrostatic component, a short-range repulsion and an attractive VDW component.

Ex.: Compute the equilibrium spacing \((r_o)\) of the Na and Cl atoms in NaCl and the lattice energy, \(V(r)\), of the crystal. Compare the computed values with the known values (on next slide).
In the physical description of the ionic bond we used a term from the L-J model to account for short-range repulsions. This was chosen mainly for consistency. However, in practice, it is common to use a repulsive parameter of the form:

\[ V_{\text{rep}}(r_{ij}) = A_{ij} e^{-r_{ij}/\rho_{ij}} \] (3)

similar in form to our previously defined repulsive force:

\[ F_{R} = \lambda e^{-r/\rho} \]

The parameters are chosen so that a model using these values reproduces known properties, with the assumption that the same model will then be capable of computing unknown properties.

When combined with an electrostatic attractive term, this is the Born-Mayer-Huggins (BMH) form of the potential energy.

Simple calculations can be carried out by hand, while calculations involving more complex structures or defects are usually carried out by computers using the BMH potential.
Return to Ionic Bonding Model
(BMH form continued)

• If we combine the repulsive parameter, eq.(3), with the Madelung attractive energy (ignoring VDW attractive part for the moment), we get the **BMH form of the potential energy**:

\[
V(r) = \frac{-ke^2\alpha(n_1 + n_2)Z_1Z_2}{2r} + NA_{ij}e^{-\frac{r}{\rho_{ij}}}
\]

(4)

• We can compute the equilibrium lattice constant (separation), \(r_o\), and lattice energy \(V(r_o)\).

• For example, from Table 7.17, a) calculate \(r_o\) and \(V(r_o)\) for MgO using only nearest neighbor repulsions, how do the values compare with Table 7.1.

**O-O repulsions and the attractive VDW component (-\(C_{ij}/r^6\)) from L-J model** [secondary effects] have little influence on the equilibrium lattice constant (separation), \(r_o\), and lattice energy \(V(r_o)\).

• Ionic pair potential calculations can be used to determine defects (point and area) in ionic compounds, e.g., NiO grain/tilt boundaries have different surface energies than inside grains; analogous to computing surface energies (\(\gamma\)) we discussed last class for FCC Cu.
Table 8.1. *The cohesive energy and melting points of the simple metals.*

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_c$ (eV)</th>
<th>$T_m$ °C</th>
<th>Z</th>
<th>$d_0$ (Å)</th>
<th>post-transition metals</th>
<th>$E_c$ (eV)</th>
<th>$T_m$ °C</th>
<th>Z</th>
<th>$d_0$ (Å)</th>
</tr>
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<tr>
<td>Li</td>
<td>1.63</td>
<td>179</td>
<td>1</td>
<td>3.040</td>
<td>Zn</td>
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<td>2</td>
<td>2.66</td>
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<tr>
<td>Na</td>
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<td>98</td>
<td>1</td>
<td>3.716</td>
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<tr>
<td>K</td>
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<td>1</td>
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<td>Hg</td>
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<td>−39</td>
<td>2</td>
<td>2.96</td>
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<tr>
<td>Rb</td>
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<td>4.936</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Cs</td>
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<td>28</td>
<td>1</td>
<td>5.265</td>
<td>In</td>
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<td>157</td>
<td>3</td>
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<tr>
<td>Be</td>
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<td>2</td>
<td>2.286</td>
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