Since the long-range mobility of ions is vanishingly small in the solid state (except for solid Helium), one can estimate the kinetic energy of the ions to be smaller than that of the electrons by a factor of $(m/M_k)^{1/2} \approx 10^{-2} - 10^{-3}$, which suggests using m/M as a perturbation parameter where M is, e.g., the smallest ion mass in the system. In the *adiabatic approximation* (Born and Oppenheimer, 1927) one treats the electronic problem for fixed ion coordinates; feeding back the electronic eigenenergies as a function of the ion coordinates then allows for an approximate treatment of the ionic contribution which reduces the error to $(m/M)^{3/4}$ (see, e.g., Czycholl, 2000). We will take the zeroth-order approximation, i.e., use immobile ions on a periodic lattice and view them as an external potential for the electrons. The effect of this considerable simplification should be kept in mind when later interpreting results, in particular with respect to transport properties.

1.1.2 Electronic Lattice Models

The resulting purely electronic Hamiltonian,

$$H = \sum_{i=1}^{N_e} \frac{\boldsymbol{p}_i^2}{2m} + \sum_i V(\boldsymbol{r}_i) + \sum_{i<j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \tag{1.2}$$

where the external potential $V(\boldsymbol{r}) = V(\boldsymbol{r} + \boldsymbol{R}_\alpha)$ is periodic on the lattice (with primitive lattice vectors $\boldsymbol{R}_\alpha$ for $\alpha = 1, \ldots, d$, where d is the dimension), defines the electronic lattice problem.

A full solution of this problem would have to include energy contributions (of positive and negative sign) of at least the highest x-ray absorption edge of the constituting atoms, which can be more than 6 orders of magnitude larger than energy differences between, e.g., metallic and insulating phases considered in this work. In this situation it is useful to distinguish between *core electrons* and *valence electrons* where the former are assumed to be tightly bound to the nuclei. The resulting new “elementary particles”, the *core ions*, then define a new, drastically weaker crystal potential. Since core ions are polarizable they also modify the infinite-range $1/r$ potential of the bare Coulomb electron-electron interaction to some shorter ranged form.[4] Provided that these effects can be quantified, we may restrict the treatment to few valence electrons per lattice site,

$$H = \sum_{i=1}^{N_v} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i=1}^{N_v} V^{\text{ion}}(\boldsymbol{r}_i) + \sum_{i=1}^{N_v-1} \sum_{j=i+1}^{N_v} V^{ee}(\boldsymbol{r}_i, \boldsymbol{r}_j), \tag{1.3}$$

where N_v is the number of valence electrons and V^{ion} the shielded lattice potential. Here, we have implicitly assumed an instantaneous effective interaction of the density-density type which is certainly not exact. We also point out that the (screened) effective interaction potential V^{ee} between valence electrons is in general neither homogeneous nor isotropic since the shielding charges are localized. Now switching

[4] Valence electrons can also take part in shielding the electron-electron interaction. This effect should, however, not be built into a microscopic valence-electron model, but result from its solution.