Crystal Physics

Textbook Hamiltonians are normally written as kinetic energy + external potential + e-e interaction.
However, crystals made of atoms contain very strong potentials (from nuclei) that bring in very high kinetic energies. Thus kinetic energy eigenfns — plane waves — are very inefficient. (This is why pseudopotentials were developed, but that's a different story.)

For efficiency, the non-interacting Hamiltonian should be based on an "effective," mean-field potential $\hat{u}_{mf}(r)$ ["mean-field" = average field seen by all electrons].

Then the kinetic energy $\hat{k}$ and $\hat{u}_{mf}$ form a one-electron problem that is diagonalized to give 1-electron band states

$$\hat{h}(r)\,\psi_{kn}(r) = \varepsilon_{kn}\,\psi_{kn}(r); \quad \text{band energies } \varepsilon_{kn}$$

The effective potential that is used in practice is the DFT Kohn-Sham potential:

$$u_{mf}(r) = v_{ext}(r) + v_h(r) + v_{ex}(r) + v_{corr}(r)$$

(Nuclei, Hartree, Exchange, Correlation)

$$= v_{ext}(r) + v_{hxc}(r)$$

The non-interacting ground state to use for the many-body problem is
all states w/ $\varepsilon_{kn} < \varepsilon_F$ occupied ("inside the Fermi surface").

The number of occupied states is equal to the number of electrons

Many-body Hamiltonian for a crystal

$$\hat{H} = \hat{K} + \hat{U}_{mf} + \hat{V} + (\hat{U} - \hat{U}_{mf}) = \hat{H}_{KS} + \Delta\hat{V}$$

$$\hat{H}_{KS} = \sum_{i=1}^{N} \hat{h}(r_i), \quad \hat{h}(r_i) = \hat{h}(r_i) + \hat{u}_{mf}(r_i), \text{ same for every electron (mean field)}$$

$$h(r)\,\psi_{kn}(r) = \varepsilon_{kn}\psi_{kn}(r); \quad \psi_{kn}(r) = e^{ik\cdot r}u_{kn}(r)$$

$$u_{mf}(r+R) = u_{mf}(r) \quad \forall \text{ direct lattice vector } R.$$

R_1, R_2, R_3 define Brillouin zone (BZ).

Complete set of states: 2 kinds

- momenta $\hbar k$ in normaliz'n box; $|k| \to \infty$
- crystal momenta $\hbar k$ in BZ + band index n, $n = 1, 2, 3, \ldots, \infty$ } this is the useful basis set

Complete set of creation operators: $c^{\dagger}_{kn\sigma}$ $(c_{kn\sigma})$

Then, in real space: $\psi^{\dagger}_{\sigma}(r) = \frac{1}{\sqrt{V}} \sum_{kn} \psi^{*}_{kn\sigma}(r)\, c^{\dagger}_{kn\sigma}$

$$\psi_{\sigma}(r) = \frac{1}{\sqrt{V}} \sum_{kn} \psi_{kn}(r)\, c_{kn\sigma}$$

Generally, expressions expressed in terms of planewave states translate simply to similar expressions involving Bloch states, but coefficients/matrix elements must be transformed appropriately.

Non-interacting system.

$$\hat{H}_0 = \sum_{kn\sigma} \varepsilon_{kn\sigma}\, c^{+}_{kn\sigma} c_{kn\sigma}\,; \quad \text{usually } \varepsilon_{kn\sigma} \to \varepsilon_{kn}$$

QM says

$$i\hbar \dot{c}^{+}_{kn\sigma} = \left[c^{+}_{kn\sigma}, \hat{H}_0 \right] = \sum_{k'n'\sigma'} \left[c^{+}_{kn\sigma} c^{+}_{k'n'\sigma'} c_{k'n'\sigma'} - c^{+}_{k'n'\sigma'} c^{+}_{k'n'\sigma'} c_{kn\sigma} \right] \varepsilon_{k'n'}$$

$$= \sum_{k'n'\sigma'} \varepsilon_{k'n'} \left[- c^{+}_{k'n'\sigma'} c_{kn\sigma} c^{+}_{k'n'\sigma'} - \{ \;\} \right]$$

$$= \sum_{k'n'\sigma'} \varepsilon_{k'n'} \left[- c^{+}_{k'n'\sigma'} \left\{ -c^{+}_{k'n'\sigma'} c_{kn\sigma} + \delta_{kk'}\delta_{nn'}\delta_{\sigma\sigma'} \right\} - \{ \;\} \right]$$

cancel

$$= \varepsilon_{kn} c^{+}_{kn\sigma} \quad \text{after applying } \delta\text{'s.}$$

so it has a very simple commutator. Solution.

$$c^{+}_{kn\sigma}(t) = c^{+}_{kn\sigma}(0)\, e^{-i\varepsilon_{kn}t/\hbar} \;;\; c_{kn\sigma}(t) = c_{kn\sigma}(0)\, e^{+i\varepsilon_{kn}t/\hbar}$$

This type of behavior corresponds to the fact that $c^{+}_{kn\sigma}$ adds (a particle with) ε_{kn} energy to the system. Trivial time dependence.

$$\hat{H} = \sum_j \varepsilon_j c_j^\dagger c_j + \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l + \sum_{ij} U_{ij} c_i^\dagger c_j$$

Calculate $[c_m^\dagger, \hat{H}] =$ (a) + (b) + (c).

(a) we know $[c_m^\dagger, \hat{H}] = \varepsilon_m$

(c) $[c_m^\dagger, c_i^\dagger c_j] = c_m^\dagger c_i^\dagger c_j - c_i^\dagger c_j c_m^\dagger = -c_i^\dagger c_m^\dagger c_j - c_i^\dagger c_j c_m^\dagger$

$= -c_i^\dagger(-c_j c_m^\dagger + \delta_{jm}) - c_i^\dagger c_j c_m^\dagger = -\delta_{jm} c_i^\dagger$

so

$$[c_m^\dagger, \sum_{ij} U_{ij} c_i^\dagger c_j] = \sum_{ij} U_{ij}(-\delta_{jm} c_i^\dagger) = -\sum_i U_{im} c_i^\dagger .$$

(b) $[c_m^\dagger, c_i^\dagger c_j^\dagger c_k c_l] = -c_i^\dagger c_m^\dagger c_j^\dagger c_k c_l - c_i^\dagger c_j^\dagger c_k c_l c_m^\dagger$

$= -c_i^\dagger(c_j^\dagger c_k c_m^\dagger - \delta_{mk} c_j) c_l - c_i^\dagger c_j^\dagger c_k c_l c_m^\dagger$

$= -c_i^\dagger c_j^\dagger c_k(\delta_{lm} - c_l c_m^\dagger) + c_i^\dagger c_j^\dagger c_l \delta_{mk} - c_i^\dagger c_j^\dagger c_k c_l c_m^\dagger$

$= c_i^\dagger c_j^\dagger(c_l \delta_{mk} - c_k \delta_{ml})$

so (V_{ijkl})

$$[c_m^\dagger, \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l] = \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger (c_l \delta_{km} - c_k \delta_{lm})$$

$$= \sum_{ijl} V_{ijml} c_i^\dagger c_j^\dagger c_l - \sum_{ijk} V_{ijkm} c_i^\dagger c_j^\dagger c_k$$

$$= \sum_{ijk} (V_{ijmk} - V_{ijkm}) c_i^\dagger c_j^\dagger c_k$$

Let's "average out" some of these many horrible terms.

Suppose we simplify $c_1^\dagger c_2 \to \langle c_1^\dagger c_2 \rangle = n_1 \delta_{1,2}$

We have the operator $c_i^\dagger c_j^\dagger c_k = -c_j^\dagger c_i^\dagger c_k$ (anticommutation)

so replace $c_i^\dagger c_j^\dagger c_k \to \frac{1}{2}\left(c_i^\dagger c_j^\dagger c_k - c_j^\dagger c_i^\dagger c_k\right)$

$$\to \frac{1}{2}\left(c_i^\dagger \langle c_j^\dagger c_k \rangle - c_j^\dagger \langle c_i^\dagger c_k \rangle\right)$$

$$= \frac{1}{2}\left(c_i^\dagger n_j \delta_{jk} - c_j^\dagger n_i \delta_{ik}\right)$$

then

$$[c_m^\dagger, \hat{V}] \approx \sum_{ijk} \left(V_{ijmk} - V_{ijkm}\right) \frac{1}{2}\left(c_i^\dagger n_j \delta_{jk} - c_j^\dagger n_i \delta_{ik}\right)$$

$$= \frac{1}{2}\sum_{ij}\left(V_{ijmj} - V_{ijjm}\right) c_i^\dagger n_j - \frac{1}{2}\sum_{ij}\left(V_{ijmj} - V_{ijim}\right) n_i c_j^\dagger$$

Switch indices on 2nd

$$= \frac{1}{2}\sum_{ij}\left(V_{ijmj} + V_{jiim} - V_{ijjm} - V_{jiim}\right) n_j c_i^\dagger$$

$$= \frac{1}{2}\sum_{i}\sum_{j}^{occ}\left(V_{ijmj} + V_{jiim} - V_{ijjm} - V_{jiim}\right) c_i^\dagger$$

$$= \sum_i \tilde{V}_{im} c_i^\dagger$$

This is the same form as (c) from the 1-body potential. Then there is an effective, mean-field correction, can be added to the original H_0 to re-diagonalize and give renormalized electrons, and a better starting point to treat actual (dynamical) interactions.