

Physics 489 S 04 Lecture 16
Methods for Calculation of Bands in Crystals
A & M Chpt. 11 and Notes

1. Independent Electron Approximation
 Schrodinger Eq.: $(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) - \epsilon_{n,\mathbf{k}})\psi_{n,\mathbf{k}}(\mathbf{r}) = 0$
 Wave function $\psi_{n,\mathbf{k}}(\mathbf{r})$ must vary rapidly near the nuclei and slowly in between nuclei.
 (valence vary more rapidly than core states (!) since they must be orthogonal to the core states) and vary slowly in between nuclei.
 Difficult to determine accurately
2. Plane wave Fourier methods (Derived before as "second" proof of Bloch Theorem)
 Basis: set of plane waves $\mathbf{k} + \mathbf{G}$
 Secular Eq.: $|H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) - \epsilon\delta_{\mathbf{G},\mathbf{G}'}| = 0$.
 Requires many plane waves ($\approx 1,000 - 100,000$) to describe $\psi_{n,\mathbf{k}}(\mathbf{r})$ near the nuclei
3. Augmented Plane Wave (APW) and Korringa-Kohn-Rostoker (KKR) methods
 Divide space into core and interstitial regions.
 "Muffin Tin potential": $V(\mathbf{r}) \approx$ spherical in each core region; \approx constant in interstitial region.
 Basis: set of plane waves $\mathbf{k} + \mathbf{G}$ outside core, each matched to spherical waves inside.
 Secular Eq.: $|H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) - \epsilon S_{\mathbf{G},\mathbf{G}'}(\mathbf{k})| = 0$.
4. Orthogonalized Plane waves (Herring)
 Basis: set of plane waves $\mathbf{k} + \mathbf{G}$, each orthogonalized to core states
 Secular Eq.: same form as above
5. Pseudopotential Method
 Replace the core region in APW with a smooth potential which gives the *same scattering properties* as the real core, but without bound core states
 Eigenstates of the smooth pseudopotential have same eigenvalues as the valence states of the all-electron case, same density outside the core regions
 $V_{core}(\mathbf{r}) \rightarrow V_{smooth}(\mathbf{r})$ in Schrodinger Eq.
 Now solve with plane waves: Not so many plane waves required!
 Justification of the "Nearly Free Electron" approach for metals.
6. How to predict the potential $V(\mathbf{r})$ or the pseudopotential $V_{smooth}(\mathbf{r})$?
 Must take into account in some way the difficult problem of the effects of the electrons on one-another!
 The modern widely-used approach is "density functional theory".