

Lecture 2

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Crystal Structure: Unit Cell (Recall)

=> The shape and translation of a unit cell are determined by its unit vectors...

- 2D: (a,b)
 Notation: Bold font used for vectors
- 3D: (a,b,c) (e.g., out of the plane below)
 Translation vactor: B-n a+n,b+n c (integers: n n)

=> Translation vector: R=n_aa+n_bb+n_cc (integers: n_{a,} n_{a,} n_c)



Unit Cell



Crystal Hamiltonian & Electron Density

=> Density Functional Theory (Kohn-Sham) approach...

$$\begin{aligned} \varepsilon_{m,k}\psi_{m,k} &= \widehat{H}\psi_{m,k} \\ & \uparrow \\ eigenenergy \\ band index, wave number \end{aligned} \\ \widehat{H} &= \begin{bmatrix} -\frac{1}{2}\nabla^2 + V(r) \\ \downarrow \\ Kinetic energy \\ potential \end{aligned} \\ \hline V(r) &= V_{ions}(r) + V_H(r) + V_{XC}(r) \end{aligned}$$

e-é, electrostatic (Hartree)

Crystal Periodicity:

nuclei

$$V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r}) \longleftrightarrow \rho(\boldsymbol{r} + \boldsymbol{R}) = \rho(\boldsymbol{r})$$



Crystal Hamiltonian & Electron Density

=> Interdependence...

$$\begin{aligned}
\varepsilon_{m,k}\psi_{m,k} &= \widehat{H}\psi_{m,k} \qquad \widehat{H} = \left[-\frac{1}{2}\nabla^{2} + V(r)\right] \\
V(r) &= V_{ions}(r) + V_{H}(r) + V_{XC}(r) \\
\hline
\rho(r) &= \frac{1}{N_{k}}\sum_{k}\sum_{m \in occ}\psi_{m,k}\psi_{m,k}^{*} \\
\hline
\rho(r) \to V_{H}(r) \\
\rho(r) \to V_{XC}(r)
\end{aligned}$$

...self-consistent loop, more in a later lecture....

K-points & Electron Density

=> Why average over k-points... delocalization....



K-points & Electron Density

=> Why average over k-points... delocalization....



K-point Sampling & Electron Density

=> k-points sampling methods....





The simplest (and most common) choice is to uniformly sample the Brillouin zone.

Technical term: o *"Mohnhorst-Pack" sampling*

K-point Sampling & Electron Density

=> Rough "unit cell" k-points sampling trends...

less k-points



more k-points

... more k-points gives a higher accuracy electron density description.

K-point Sampling & Total Energy

=> Ex: Diamond lattice k-point sampling trends...



Total Energy Dependence on Electron Density

=> Electron-electron (e-e), ion-ion, and electron-ion interactions...



Total Energy To Binding Properties

=> Similar diatomic interaction form for all atoms...



Crystal Structure: Unit Cell (Recall)

=> The shape and translation of a unit cell are determined by its unit vectors...

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Unit Cell



Electron Density Repetition & Crystals

=> When the electron density and nuclear positions are periodic...

$$\rho(\mathbf{r}) = \frac{1}{N_k} \sum_{k} \sum_{m \in occ} \psi_{m,k} \psi_{m,k}^*$$

$$\rho(\mathbf{r} + \mathbf{R}) = \rho(\mathbf{r})$$
Imposes k-point sampling requirement
$$\psi_{m,k}(\mathbf{r}) = e^{+i\mathbf{k}\cdot\mathbf{r}} u_{m,k}(\mathbf{r})$$
Lattice periodic component...
$$u_{m,k}(\mathbf{r} + \mathbf{R}) = u_{m,k}(\mathbf{r})$$

Periodicity in the Bloch Wave



Periodicity in the Crystal Potential



Fourier Series Expansion of Bloch Wave



Fourier Series Expansion of Potential



General Fourier Expansion

...
$$V(r + R) = V(r)$$

$$V(r) = \sum_{\alpha} V(G_{\alpha})e^{+iG_{\alpha} \cdot r} \int V(G_{\alpha}) = \frac{1}{\Omega} \int_{\Omega} V(r)e^{-iG_{\alpha} \cdot r} dr$$

Plane wave expansion:

$$\psi_{m,k}(r) = e^{+ik \cdot r} u_{m,k}(r)$$

$$\psi_{m,k}(r) = e^{+ik \cdot r} \sum_{\alpha} u_{m,k}(G_{\alpha}) e^{+iG_{\alpha} \cdot r}$$

$$\psi_{m,k}(r) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(k) e^{+iq \cdot r}$$

$$q = k + G_{\alpha}$$

Plane Waves

$$|\mathbf{q}\rangle = \frac{1}{\sqrt{\Omega}} e^{+i\mathbf{q}\cdot\mathbf{r}} \quad \mathbf{q} = \mathbf{k} + \mathbf{G}_{\alpha}$$

$$|\mathbf{q}'\rangle = \frac{1}{\sqrt{\Omega}} e^{+i\mathbf{q}'\cdot\mathbf{r}} \quad \mathbf{q}' = \mathbf{k} + \mathbf{G}_{\alpha'}$$
orthogonal
$$\langle \mathbf{q}'|\mathbf{q}\rangle = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{q}'\cdot\mathbf{r}} e^{+i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \delta_{\mathbf{q},\mathbf{q}'}^{\mathbf{r}}$$

$$\widehat{H} = \left[-\frac{1}{2}\nabla^{2} + V(\mathbf{r})\right] \quad \text{Hamiltonian operator}$$

$$\left\langle \mathbf{q}' \left| -\frac{1}{2}\nabla^{2} \right| \mathbf{q} \right\rangle = \frac{1}{2} |\mathbf{q}|^{2} \delta_{\mathbf{q},\mathbf{q}'} \quad \langle \mathbf{q}'|V(\mathbf{r})|\mathbf{q}\rangle = \sum_{\alpha''} V(\mathbf{G}_{\alpha''}) \delta_{\mathbf{q}-\mathbf{q}',\mathbf{G}_{\alpha''}}$$

$$H_{\alpha,\alpha'}(\mathbf{k}) = \langle \mathbf{q}' \left| \widehat{H} \right| \mathbf{q} \rangle = \langle \mathbf{k} + \mathbf{G}_{\alpha} \left| \widehat{H} \right| \mathbf{k} + \mathbf{G}_{\alpha'} \rangle$$

$$= \frac{1}{2} |\mathbf{k} + \mathbf{G}_{\alpha}|^{2} \delta_{\alpha,\alpha'} + V(\mathbf{G}_{\alpha} - \mathbf{G}_{\alpha'}) \int_{\mathbf{q}}^{\mathbf{H}} \frac{\mathbf{H}_{\alpha}}{\mathbf{H}_{\alpha}}$$

Plane Wave Matrix for each k-point



Diagonalize and Solve at Many K-points

$$H_{\alpha,\alpha'}(\mathbf{k}) = \frac{1}{2} |\mathbf{k} + \mathbf{G}_{\alpha}|^{2} \delta_{\alpha,\alpha'} + V(\mathbf{G}_{\alpha} - \mathbf{G}_{\alpha'})$$

$$[H(\mathbf{k})]\{c_{m,q}(\mathbf{k})\} = \varepsilon_{m}(\mathbf{k})\{c_{m,q}(\mathbf{k})\} \leftarrow vector 1 \times N$$
matrix $N \times N$

$$\psi_{m,k} = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{+iq \cdot r} \rho(r) = \frac{1}{N_{k}} \sum_{k} \sum_{m \in occ} \psi_{m,k} \psi_{m,k}^{*}$$

$$q = \mathbf{k} + \mathbf{G}_{\alpha}$$

$$Key \ computing \ problem$$

$$\sim O(N^{3})$$

$$\downarrow plane \ waves$$

$$N$$

$$\sum_{r = 1}^{10} \sum_{q = 1}^{10} \sum_{r = 1}^{10$$

Defects in Crystals: Supercells

=> All of these periodic expansion methods can also be applied to study defects and even chemical reactions (as an array of periodic



Defects in Crystals: Supercells

=> Many types of defects can be studied with supercells....



...HW: with a linear increase in each dimension, the number of sampling k-points needed decreases linearly (zone folding).

Back to the Matrix Problem...

$$H_{\alpha,\alpha'}(\mathbf{k}) = \frac{1}{2} |\mathbf{k} + \mathbf{G}_{\alpha}|^{2} \delta_{\alpha,\alpha'} + V(\mathbf{G}_{\alpha} - \mathbf{G}_{\alpha'})$$

$$[H(\mathbf{k})]\{c_{m,q}(\mathbf{k})\} = \varepsilon_{m}(\mathbf{k})\{c_{m,q}(\mathbf{k})\} \leftarrow vector 1 \times N$$

$$\psi_{m,k} = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{+iq\cdot r} - \rho(\mathbf{r}) = \frac{1}{N_{k}} \sum_{k} \sum_{meocc} \psi_{m,k} \psi_{m,k}^{*}$$

$$q = \mathbf{k} + \mathbf{G}_{\alpha}$$

$$(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{+iq\cdot r} - \rho(\mathbf{r}) = \frac{1}{N_{k}} \sum_{k} \sum_{meocc} \psi_{m,k} \psi_{m,k}^{*}$$

$$(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{+iq\cdot r} - \rho(\mathbf{r}) = \frac{1}{N_{k}} \sum_{k} \sum_{meocc} \psi_{m,k} \psi_{m,k}^{*}$$

$$(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{-iq\cdot r} - \frac{1}{N_{k}} \sum_{k} \sum_{meocc} \psi_{m,k} \psi_{m,k}^{*}$$

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$$(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{-iq\cdot r} - \frac{1}{N_{k}} \sum_{q} \sum_{meocc} \psi_{m,k} \psi_{m,k}^{*}$$

$$(\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{q} c_{m,q}(\mathbf{k})e^{-iq\cdot r} - \frac{1}{N_{k}} \sum_{q} \sum_{q} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} \psi_{m,k}^{*} - \frac{1}{N_{k}} \sum_{q} \psi_{m,k} - \frac{1}{N_{k}} \sum_{q} \psi_{m$$

Reducing the Matrix Size

=> The "true" lattice potential is actually very sharp, requiring many plane waves to represent in a plane wave basis...



Reducing the Matrix Size

=> Recall the "ion-core" approximation...



=> A much smoother potential can be represented by much fewer plane waves in Fourier transform...

Towards Pseudopotentials

=> Scattering errors (etc.) from "just" an "ion-core" ...



=> Introduce non-local term to fix scattering & other properties in the ion-core approximation...

$$\widehat{H} = \begin{bmatrix} -\frac{1}{2}\nabla^{2} + V_{ic}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{XC}(\mathbf{r}) + \widehat{V}_{nl} \end{bmatrix}$$
"ion-core"

Reducing the Matrix Size

=> Revised Hamiltonian to reduce the number of plane waves (matrix size)....

$$\widehat{H} = \begin{bmatrix} -\frac{1}{2} \nabla^2 + V_{ic}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + \widehat{V}_{nl} \end{bmatrix}$$
valence electrons
$$V(\mathbf{r}) = V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + \widehat{V}_{ps}$$
frozen core electrons &
$$\widehat{V}_{ps} = V_{ic}(\mathbf{r}) + \widehat{V}_{nl} \end{bmatrix}$$
Pseudopotential: smoother than bare
nuclear potential

=> Pseudopotentials are constructed in the atomic limit....



=> Recall, atomic orbitals have the general form...



... with orthogonality imposed by radial and angular oscillations.

=> A pseudopotential equals an all-electron orbital beyond a cutoff...



U used to distinguish potential (V) in the atomic limit

=> One approach is to create a separate "pseudopotential" for each atomic orbital (angular momentum s,p,d,etc.)...



... if the radial wavefunction is nodeless and smooth, so also will its pseudopotential.

=> The fitted pseudowavefunction must obey the below "rules"...



R. Martin, "Electronic Structure: Basic Theory and Practical Methods"

=> From the pseudowavefunction the pseudopotential is constructed for each scattering state....



=> Kerker or Troullier-Martins pseudopotential fits....



... but there are many types of pseudopotentials. Projector augmented waves are a variation on this theme, more common in typical planewave codes (e.g., VASP).

=> Using the Kerker method the fit would take the form...



...more accurate methods are now commonly used (illustrative only).

=> Creating an effective ion-core (many possible variations)...



=> Valence charge potential contributions (one atom)....



=> Subtract out from the orbital pseudopotential....

$$U_l^{ps} = \varepsilon_{nl} - \frac{1}{2} \left[\frac{l(l+1)}{r} - \frac{1}{R_{nl}^{ps}} \left(\nabla^2 R_{nl}^{ps} \right) \right]$$

 $\delta U_l^{ps} = U_l^{ps} - U_{ic} - U_H \left[\rho_{val} \right] - U_{XC} \left[\rho_{val} \right]$

=> Insert and reconstruct single-atom Hamiltonian....

$$\widehat{H} = \left[-\frac{1}{2} \nabla^{2} + U_{ic}(\mathbf{r}) + U_{H}[\rho_{val}] + U_{XC}[\rho_{val}] + \widehat{U}_{ps} \right]$$

$$non - local \quad \left[\widehat{U}_{ps} = \sum_{lm} \frac{|\psi_{lm}^{ps}\rangle \delta U_{l}^{ps} \langle \psi_{lm}^{ps}|}{\langle \psi_{lm}^{ps} | \psi_{lm}^{ps} \rangle} \right]^{projection}$$

$$R. Martin, "Electronic Structure: Basic Theory and Practical Methods"$$

.... non-locality also enters in the potential Fourier transform (HW).

=> The general crystal Hamiltonian then becomes...

valence electrons all atoms

$$\widehat{H} = \begin{bmatrix} -\frac{1}{2}\nabla^{2} + V_{ic}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{XC}(\mathbf{r}) + \widehat{V}_{nl} \end{bmatrix}$$

centred at each atom
$$V_{ic}(\mathbf{r}) = \sum_{j} U_{ic,j} \qquad \widehat{V}_{nl}(\mathbf{r}) = \sum_{j} \widehat{U}_{ps,j} \qquad \text{atom index}$$

=> Improper pseudopotential construction & "ghost states"....



Ex: "Ghost States for separable, norm – conserving, ab initio pseudopotentails", Phys. Rev. B 41, 12264 (1990)

Consequence: unphysical material properties computed.

... somewhat of an "art" requires transferability testing!

Crystals & Electron Waves

=> Previous Lecture Takeaways....

- Periodicity in the lattice gives rise to periodicity in the electron density;
- Electrons "move" as waves on crystal lattices;
- The energies of various electron wavevectors, band structure, gives important electronic structure (metal, semiconductor, insulator) and optical information.

=> This Lecture Takeaways....

- Electron density periodicity in the unit cell can be solved in a plane wave expansion (other expansions in another lecture)...
- This can also be done for supercells to study defects (etc.).
- Core electrons and nuclear potentials require a very large basis set to represent accurately, hence the use of pseudopotentials (to reduce the matrix size)...
- Computational scaling is a constant challenge in DFT, basic matrix inversion/diagonalization to obtain the wavefunction eigenvalues and eigenvectors scales as O(N³) or so.
 pardon typos/errors within.