

PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 17:
Reading: Chapter 10 in MPM
Ingredients of electronic structure calculations

- 1. Plane wave basis sets**
- 2. Evaluation of matrix elements**
- 3. Construction of pseudopotentials**

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9	Wed: 02/04/2015	Chap. 8	Electronic structure, LCAO and tight binding	#9	02/06/2015
10	Fri: 02/06/2015	Chap. 8	Band structure examples	#10	02/09/2015
11	Mon: 02/09/2015	Chap. 9	Electron-electron interactions	#11	02/11/2015
12	Wed: 02/11/2015	Chap. 9	Electron-electron interactions	#12	02/13/2015
13	Fri: 02/13/2015	Chap. 9	Electron-electron interactions	#13	02/16/2015
14	Mon: 02/16/2015	Chap. 10	Electronic structure calculation methods	#14	02/18/2015
15	Wed: 02/18/2015	Chap. 10	Electronic structure calculation methods	#15	02/20/2015
16	Fri: 02/20/2015	Chap. 10	Electronic structure calculation methods	#16	02/23/2015
17	Mon: 02/23/2015	Chap. 10	Electronic structure calculation methods	#17	02/25/2015
18	Wed: 02/25/2015	Chap. 10	Electronic structure calculation methods	#18	02/27/2015
19	Fri: 02/27/2015	Chap. 1-3,7-10	Review; Take-home exam distributed		
	Mon: 03/02/2015	APS Meeting	Take-home exam (no class meeting)		
	Wed: 03/04/2015	APS Meeting	Take-home exam (no class meeting)		
	Fri: 03/06/2015	APS Meeting	Take-home exam (no class meeting)		
	Mon: 03/09/2015	Spring break			
	Wed: 03/11/2015	Spring break			
	Fri: 03/13/2015	Spring break			
20	Mon: 03/16/2015				

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Some practical considerations in electronic structure calculations

Bloch theorem

$$\Psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

Plane wave representation

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$



In practice, summation is truncated:

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \leq E_{cut}$$

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Kohn-Sham equations (assuming "local" potential)

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(\mathbf{r}) \right) \Psi_{nk}(\mathbf{r}) = E_{nk} \Psi_{nk}(\mathbf{r})$$

$$V_{\text{eff}}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}_{\text{eff}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\tilde{V}_{\text{eff}}(\mathbf{G}) = \int d^3r V_{\text{eff}}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}$$

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Digression on evaluation of the Fourier transform of the effective potential

Useful identity:

$$e^{-i\mathbf{G}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^{-l} j_l(Gr) Y_{lm}^*(\hat{\mathbf{G}}) Y_{lm}(\hat{\mathbf{r}})$$

Suppose

$$V_{\text{eff}}(\mathbf{r}) = \sum_{\mathbf{a}} V^a(\mathbf{r} - \boldsymbol{\tau}^a - \mathbf{T})$$

$$\begin{aligned} \tilde{V}_{\text{eff}}(\mathbf{G}) &= \int d^3r V_{\text{eff}}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \\ &= \sum_{\mathbf{a}} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}^a} \tilde{V}^a(\mathbf{G}) \end{aligned}$$

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Digression on evaluation of the Fourier transform of the effective potential

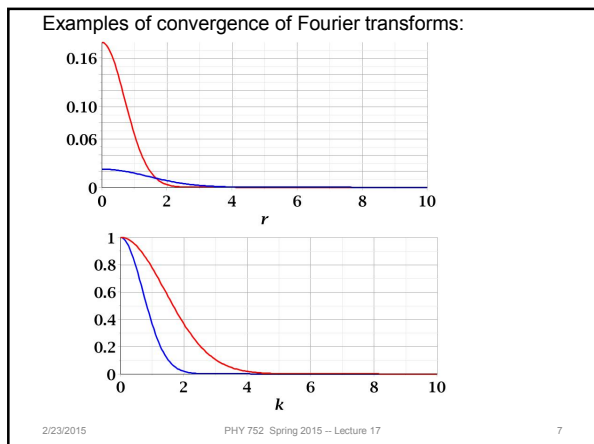
$$\tilde{V}_{\text{eff}}(\mathbf{G}) = \sum_{\mathbf{a}} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}^a} \tilde{V}^a(\mathbf{G})$$

$$\tilde{V}^a(\mathbf{G}) = 4\pi \sum_{lm} i^{-l} Y_{lm}^*(\hat{\mathbf{G}}) \int d^3r V^a(\mathbf{r}) j_l(Gr) Y_{lm}(\hat{\mathbf{r}})$$

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Convergence of plane wave expansions

$$\Psi_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} C_{nk}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$(|\mathbf{k}+\mathbf{G}| < \sqrt{2mE_{cut}/\hbar^2})$$

Electron density:

$$n(\mathbf{r}) = 2 \sum_{nk \text{ (occ)}} |\Psi_{nk}(\mathbf{r})|^2$$

$$= 2 \sum_{nk \text{ (occ)}} \left| \sum_{\mathbf{G}} C_{nk}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \right|^2$$

$$= \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$|\mathbf{G}| \leq 2\sqrt{2mE_{cut}/\hbar^2}$$

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Some practical tricks

Evaluate periodic portion of wavefunction using FFT

$$u_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} C_{nk}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

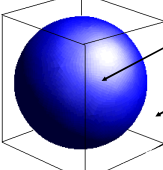
Evaluate density on real-space grid

$$n(\mathbf{r}) = 2 \sum_{nk \text{ (occ)}} |u_{nk}(\mathbf{r})|^2$$

Fourier space representation of density can be determined by inverse FFT

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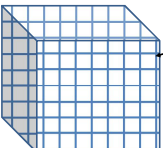
FFT grid size **Reciprocal space**



$|\mathbf{G}| \leq G_{max}$

Enclusing parallelepiped
 $\mathbf{G} = n_1\mathbf{G}_1 + n_2\mathbf{G}_2 + n_3\mathbf{G}_3$
 $0 \leq n_i \leq N_i$

Real space grid points



$\mathbf{r} = \frac{m_1}{N_1}\mathbf{T}_1 + \frac{m_2}{N_2}\mathbf{T}_2 + \frac{m_3}{N_3}\mathbf{T}_3$

$\mathbf{G} \cdot \mathbf{r} = 2\pi \left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3} \right)$

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FFT equations <http://www.fftw.org/>

$$f(n_1, n_2, n_3) = \sum_{m_1, m_2, m_3} \tilde{f}(m_1, m_2, m_3) e^{i2\pi \left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3} \right)}$$

$$\tilde{f}(m_1, m_2, m_3) = \frac{1}{N_1 N_2 N_3} \sum_{n_1, n_2, n_3} f(n_1, n_2, n_3) e^{-i2\pi \left(\frac{n_1 m_1}{N_1} + \frac{n_2 m_2}{N_2} + \frac{n_3 m_3}{N_3} \right)}$$

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How can we construct a pseudopotential?

Norm-conserving pseudopotentials

VOLUME 43, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1979

Norm-Conserving Pseudopotentials
 D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974
 (Received 1 August 1979)

A very simple procedure to extract pseudopotentials from *ab initio* atomic calculations is presented. The pseudopotentials yield exact eigenvalues and nodless eigenfunctions which agree with atomic wave functions beyond a chosen radius r_c . Moreover, logarithmic derivatives of real and pseudo wave functions and their first energy derivatives agree for $r > r_c$, guaranteeing excellent transferability of the pseudopotentials.

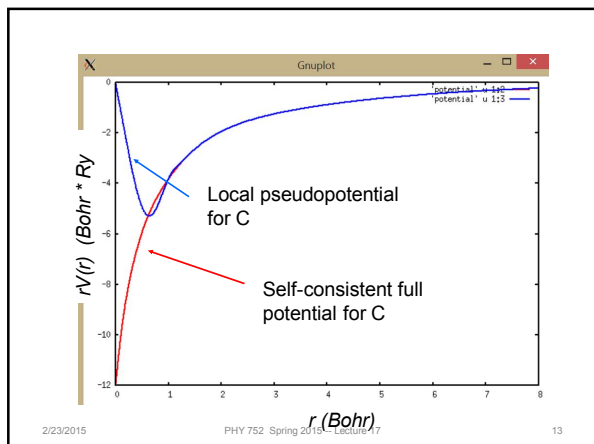
J. Phys. C: Solid St. Phys., 13 (1980) L189-94. Printed in Great Britain

LETTER TO THE EDITOR

Non-singular atomic pseudopotentials for solid state applications

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Construction methods used in ATOMPAW code

The all-electron basis functions $|\phi_i(\mathbf{r})\rangle$ are valence and continuum eigenstates of the Kohn-Sham[8] Hamiltonian.

$$H(\mathbf{r})|\phi_i(\mathbf{r})\rangle = \varepsilon_i|\phi_i(\mathbf{r})\rangle, \quad (2)$$

The Hamiltonian takes the form:

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r}), \quad (3)$$

where the self-consistent valence density $n(r)$ enters through the effective potential:

$$v_{\text{eff}}(r) \equiv -\frac{Ze^2}{r} + e^2 \int d^3r' \frac{n_{\text{core}}(r') + n(r')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{\text{xc}}[n_{\text{core}}(r) + n(r)]. \quad (4)$$

Here Z denotes the nuclear charge. The function μ_{xc} denotes the exchange correlation functional. In the present work, we used the local density approximation (LDA) form of Perdew and Wang[9], but other forms can be easily added to the code. Self-consistency implies that the valence density and the valence basis functions are related according to:

$$n(r) = \sum_{n_i l_i} o_{n_i l_i} \frac{|\phi_{n_i l_i}(r)|^2}{4\pi r^2}, \quad (5)$$

where $o_{n_i l_i}$ denotes the occupancy of the orbital " $n_i l_i$ " which can be zero, especially for generalized functions.

The pseudowavefunction is chosen to have the form:

$$\tilde{\phi}(r) = \begin{cases} r^{L+1} f(r) & \text{for } r \leq r_c \\ \phi(r) & \text{for } r > r_c. \end{cases} \quad (6)$$

Here $\phi(r)$ represents a chosen continuum wavefunction of the all-electron Hamiltonian at energy E . The function $f(r)$ is chosen to have the form

$$f(r) = e^{p(r)}, \quad (7)$$

where $p(r)$ is chosen to be an even 12^{th} order polynomial:

$$p(r) = \sum_{m=0}^6 C_m r^{2m}. \quad (8)$$

functions. The screened norm-conserving pseudopotential can be determined from polynomial according to

$$V^{PS}(r) = E + \frac{\hbar^2}{2m} \left(\frac{d^2 p}{dr^2} + \left(\frac{dp}{dr} \right)^2 + \frac{2(L_x + 1)}{r} \frac{dp}{dr} \right). \quad (9)$$

By construction, this function and its first two derivatives are equal to $v_{eff}(r)$ for $r \geq r_c$.

At this point, we can construct a smooth pseudo-Hamiltonian analogous the all-electron Hamiltonian (2) of the form

$$\hat{H}(r) \equiv -\frac{\hbar^2}{2m} \nabla^2 + V^{PS}(r). \quad (10)$$

Properties of pseudopotential and corresponding pseudo-wavefunctions

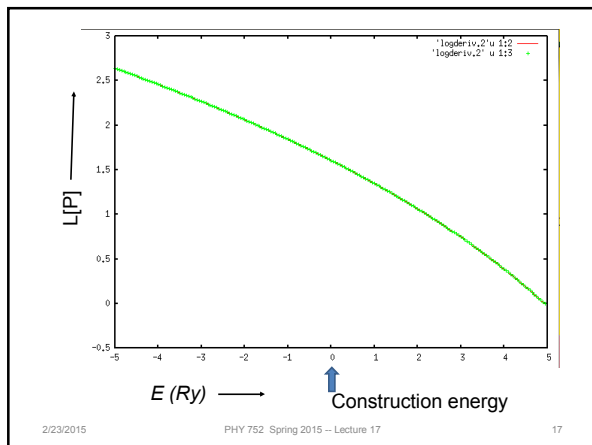
→ Correct logarithmic derivatives at energy E and at nearby energies

$$L[P_{nl}(r_c)] \equiv \frac{d}{dr} \ln([P_{nl}(r)]) \Big|_{r_c} = \frac{1}{P_{nl}(r_c)} \frac{dP_{nl}(r)}{dr} \Big|_{r_c}$$

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Useful relationship in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} \right) + V_{eff}(r) \right) P_{n,l_i}(r) = E_{n,l_i} P_{n,l_i}(r)$$

Formally take energy derivative:

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} \right) + V_{eff}(r) - E_{n,l_i} \right) \frac{dP_{n,l_i}(r)}{dE_{n,l_i}} = P_{n,l_i}(r)$$

$$-\left(P_{n,l_i}(r) \right)^2 \frac{d}{dE_{n,l_i}} L[P_{n,l_i}(r)] \Big|_{r_c} = \int_0^{r_c} dr \left(P_{n,l_i}(r) \right)^2$$

The construction ensures that

→ PS and AE have same log derivatives near E

→ What about other partial waves? (Non-local contributions to pseudopotential)

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