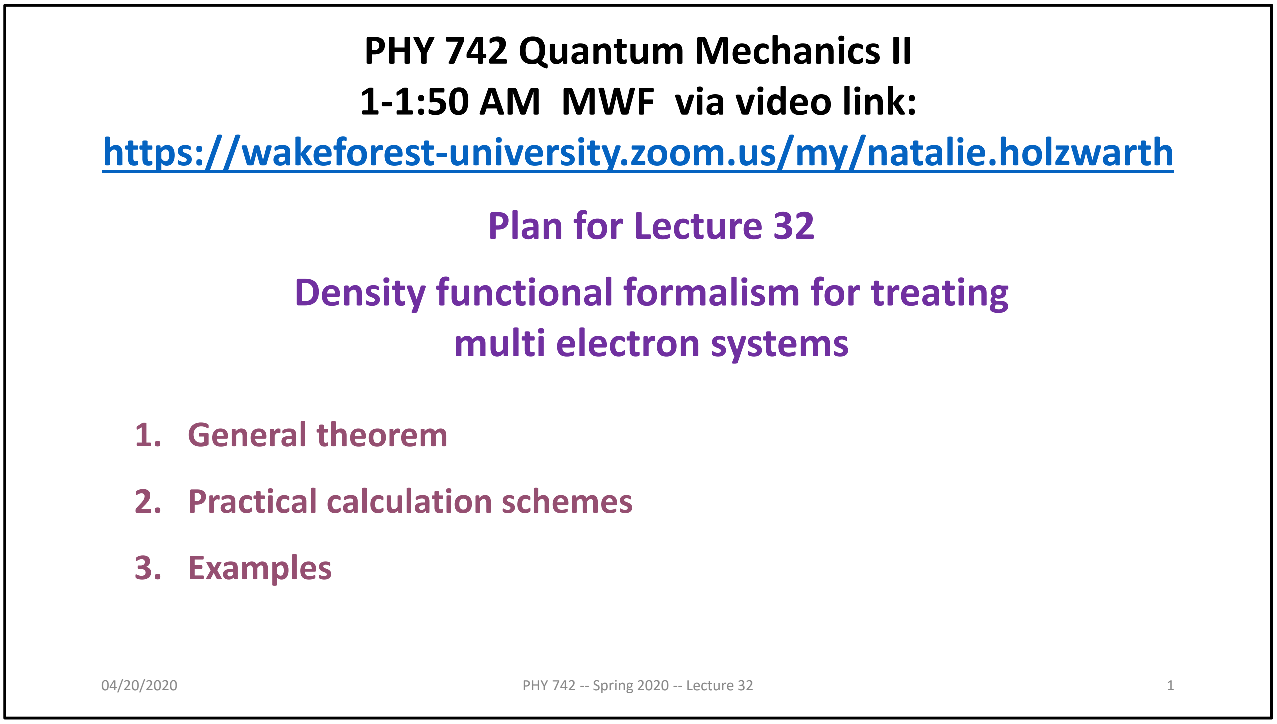


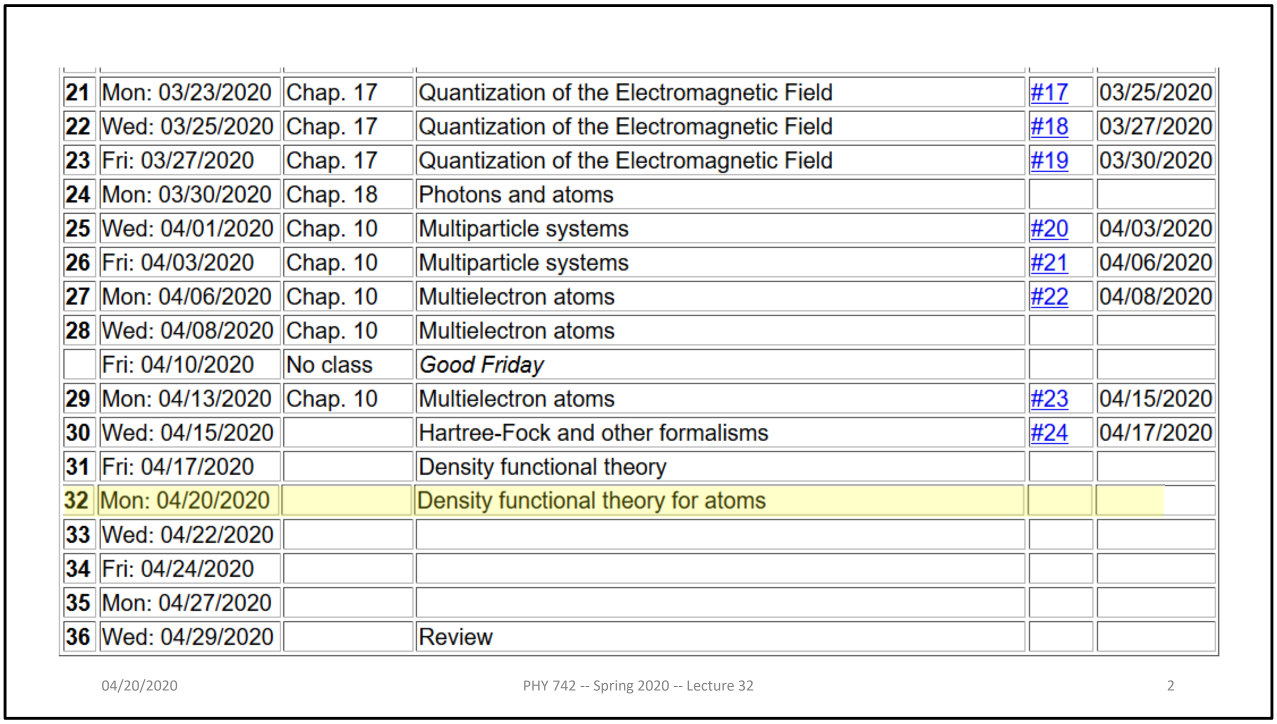
# PHY 742 Quantum Mechanics II
1-1:50 AM MWF via video link:
https://wakeforest-university.zoom.us/my/natalie.holzwarth

## Plan for Lecture 32

## Density functional formalism for treating multi electron systems

1. General theorem
2. Practical calculation schemes
3. Examples

We will illustrate the details of density functional theory for atoms.



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|---|---|---|---|---|---|
| **21** | Mon: 03/23/2020 | Chap. 17 | Quantization of the Electromagnetic Field | #17 | 03/25/2020 |
| **22** | Wed: 03/25/2020 | Chap. 17 | Quantization of the Electromagnetic Field | #18 | 03/27/2020 |
| **23** | Fri: 03/27/2020 | Chap. 17 | Quantization of the Electromagnetic Field | #19 | 03/30/2020 |
| **24** | Mon: 03/30/2020 | Chap. 18 | Photons and atoms | | |
| **25** | Wed: 04/01/2020 | Chap. 10 | Multiparticle systems | #20 | 04/03/2020 |
| **26** | Fri: 04/03/2020 | Chap. 10 | Multiparticle systems | #21 | 04/06/2020 |
| **27** | Mon: 04/06/2020 | Chap. 10 | Multielectron atoms | #22 | 04/08/2020 |
| **28** | Wed: 04/08/2020 | Chap. 10 | Multielectron atoms | | |
| | Fri: 04/10/2020 | No class | *Good Friday* | | |
| **29** | Mon: 04/13/2020 | Chap. 10 | Multielectron atoms | #23 | 04/15/2020 |
| **30** | Wed: 04/15/2020 | | Hartree-Fock and other formalisms | #24 | 04/17/2020 |
| **31** | Fri: 04/17/2020 | | Density functional theory | | |
| **32** | Mon: 04/20/2020 | | Density functional theory for atoms | | |
| **33** | Wed: 04/22/2020 | | | | |
| **34** | Fri: 04/24/2020 | | | | |
| **35** | Mon: 04/27/2020 | | | | |
| **36** | Wed: 04/29/2020 | | Review | | |

Ongoing schedule

**Summary of results for density functional theory –**

**For a system with a given one-electron potential v(r), there is a unique density n(r) which describes the system in its ground state. Although the density n(r) is a collective property of the system, it can be described by a single particle function and it implies that the task of finding the electronic ground state of the multi electron system can be mapped to a process of solving a related single particle problem self-consistently.**

Total energy

$$\mathrm{E}_{KS}(n(\mathbf{r})) = \mathrm{E}_{kin}(n(\mathbf{r})) + \mathrm{E}_{\mathbf{v}}(n(\mathbf{r})) + \mathrm{E}_{Hartree}(n(\mathbf{r})) + \mathrm{E}_{xc}(n(\mathbf{r}))$$

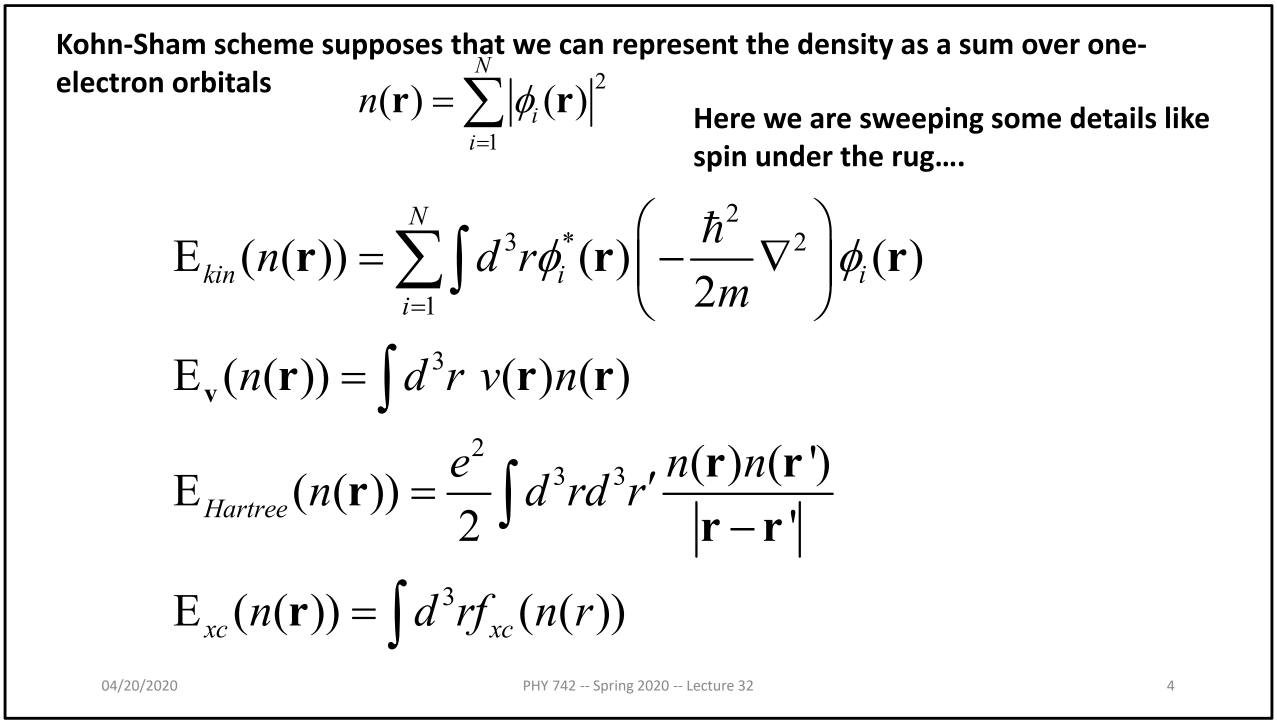
**Kinetic energy**

**Single particle interaction**

**Electron-electron repulsion**

**Exchange-correlation energy**

Summary of the theorem and of the various energy contributions.



**Kohn-Sham scheme supposes that we can represent the density as a sum over one-electron orbitals**

$$n(\mathbf{r}) = \sum_{i=1}^{N} \left|\phi_i(\mathbf{r})\right|^2$$

**Here we are sweeping some details like spin under the rug….**

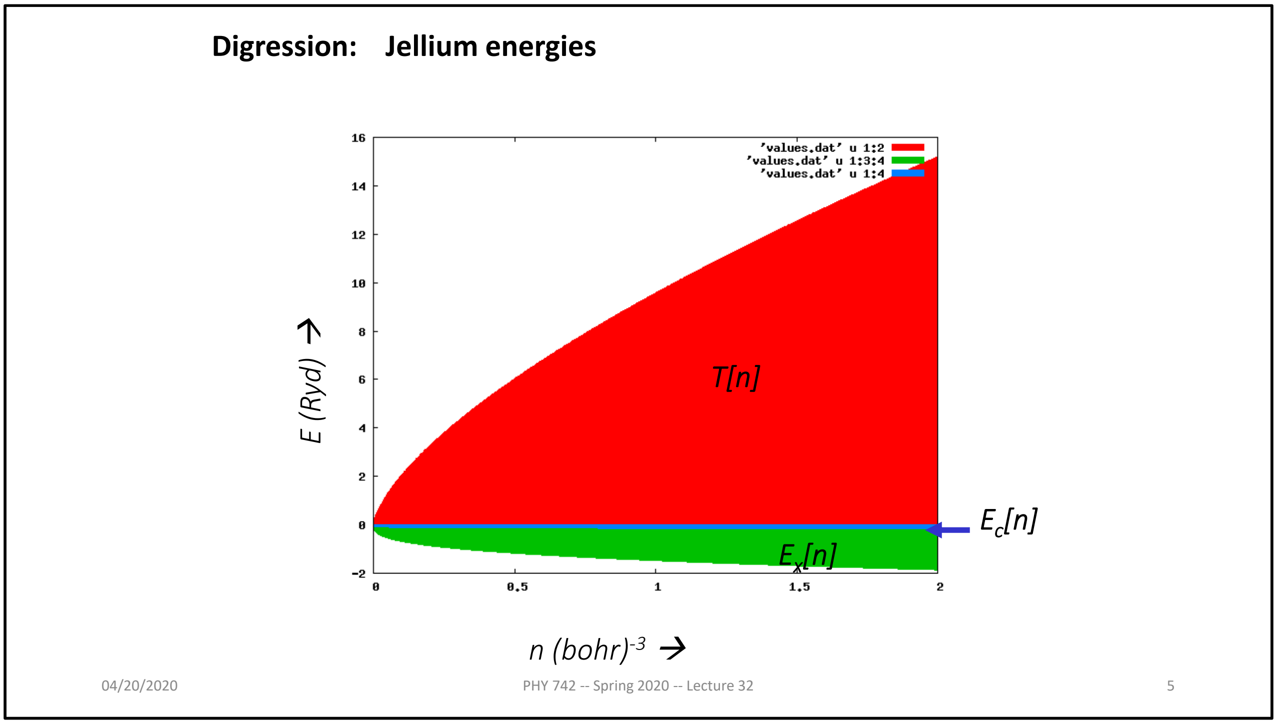
$$\mathrm{E}_{kin}(n(\mathbf{r})) = \sum_{i=1}^{N} \int d^3r \phi_i^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m}\nabla^2 \right) \phi_i(\mathbf{r})$$

$$\mathrm{E}_{\mathbf{v}}(n(\mathbf{r})) = \int d^3r \; v(\mathbf{r}) n(\mathbf{r})$$

$$\mathrm{E}_{Hartree}(n(\mathbf{r})) = \frac{e^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|}$$

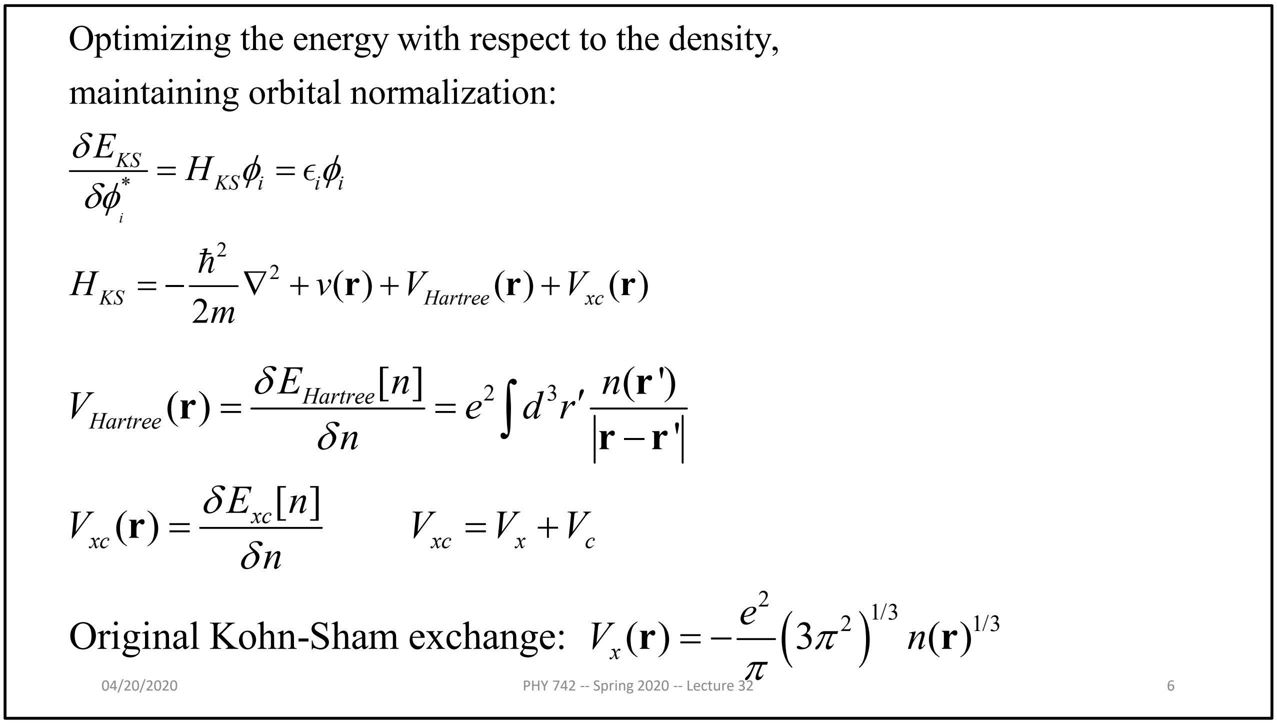
$$\mathrm{E}_{xc}(n(\mathbf{r})) = \int d^3r f_{xc}(n(r))$$

Here are the formulas for the various contributions



## Digression: Jellium energies

This gives an idea of the order of magnitude of the terms as a function of density for the jellium model



Optimizing the energy with respect to the density,
maintaining orbital normalization:

$$\frac{\delta E_{KS}}{\delta \phi_i^*} = H_{KS}\phi_i = \epsilon_i \phi_i$$

$$H_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$V_{Hartree}(\mathbf{r}) = \frac{\delta E_{Hartree}[n]}{\delta n} = e^2 \int d^3r' \, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n} \qquad V_{xc} = V_x + V_c$$

Original Kohn-Sham exchange: $V_x(\mathbf{r}) = -\frac{e^2}{\pi}\left(3\pi^2\right)^{1/3} n(\mathbf{r})^{1/3}$

Various potential terms.

## Numerical methods for solving the Kohn-Sham equations

### Self-consistent solution

Iteration $\alpha = 0$

$$\left\{ \phi_i^{\alpha}(\mathbf{r}) \right\}$$

$$n^{\alpha}(\mathbf{r}) = \sum_i \left| \phi_i^{\alpha}(\mathbf{r}) \right|^2$$

$$H_{KS}^{\alpha}(\mathbf{r}) \phi_i^{\alpha+1}(\mathbf{r}) = \epsilon_i \phi_i^{\alpha+1}(\mathbf{r})$$

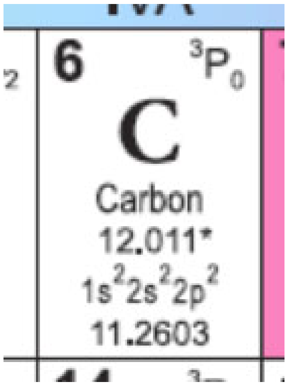
$$n_{temp}^{\alpha+1}(\mathbf{r}) = \sum_i \left| \phi_i^{\alpha+1}(\mathbf{r}) \right|^2$$

$$n^{\alpha+1}(\mathbf{r}) = x n_{temp}^{\alpha+1}(\mathbf{r}) + (1-x) n^{\text{\textbackslash alpha}}(\mathbf{r})$$

$$\alpha + 1 \Rightarrow \alpha$$

Iteration scheme

**Numerical methods for solving the Kohn-Sham equations –**
**Consider the case of a single atom, choosing the coordinate system at the center of the nucleus. We will further assume that the atom is spherically symmetric, averaging over the multiplet configurations.**



$$n(\mathbf{r}) = n(r)$$

$$\phi_i(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

$$n(r) = 4\pi \sum_i w_{n_i l_i} \left|\phi_{n_i l_i}(r)\right|^2$$

$$\text{where } \; 0 \le w_{n_i l_i} \le 2(2l_i + 1)$$

Example of Carbon atom

**Kohn-Sham equations for spherical atom**

Equations for radial orbitals $\phi_{n_i l_i}(r)$:

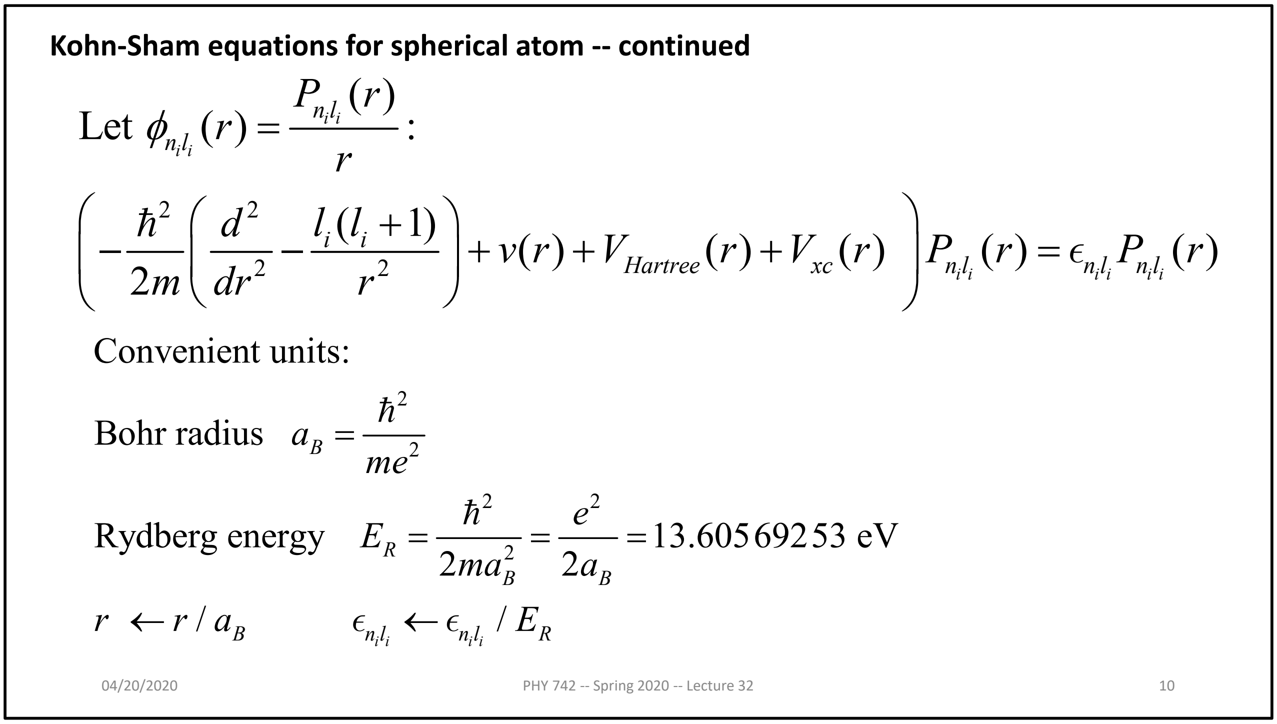
$$\left(-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r-\frac{l_i(l_i+1)}{r^2}\right)+v(r)\ +V_{Hartree}(r)+V_{xc}(r)\ \right)\phi_{n_i l_i}(r)=\epsilon_{n_i l_i}\phi_{n_i l_i}(r)$$

$$v(r)=-\frac{Ze^2}{r}$$

$$V_{Hartree}(r)=\frac{\delta E_{Hartree}[n]}{\delta n}=e^2\left(\frac{1}{r}\int_0^r r'^2\,dr' n(r')+\int_r^\infty r'\,dr' n(r')\right)$$

$$V_{xc}(r)=\frac{\delta E_{xc}[n]}{\delta n}=-\frac{e^2}{\pi}\left(3\pi^2\right)^{1/3}n(r)^{1/3}+V_c(r)$$

Detailed equations



**Kohn-Sham equations for spherical atom -- continued**

Let $\phi_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r}$:

$$\left( -\frac{\hbar^2}{2m}\left( \frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) + v(r) + V_{Hartree}(r) + V_{xc}(r) \right) P_{n_i l_i}(r) = \epsilon_{n_i l_i} P_{n_i l_i}(r)$$

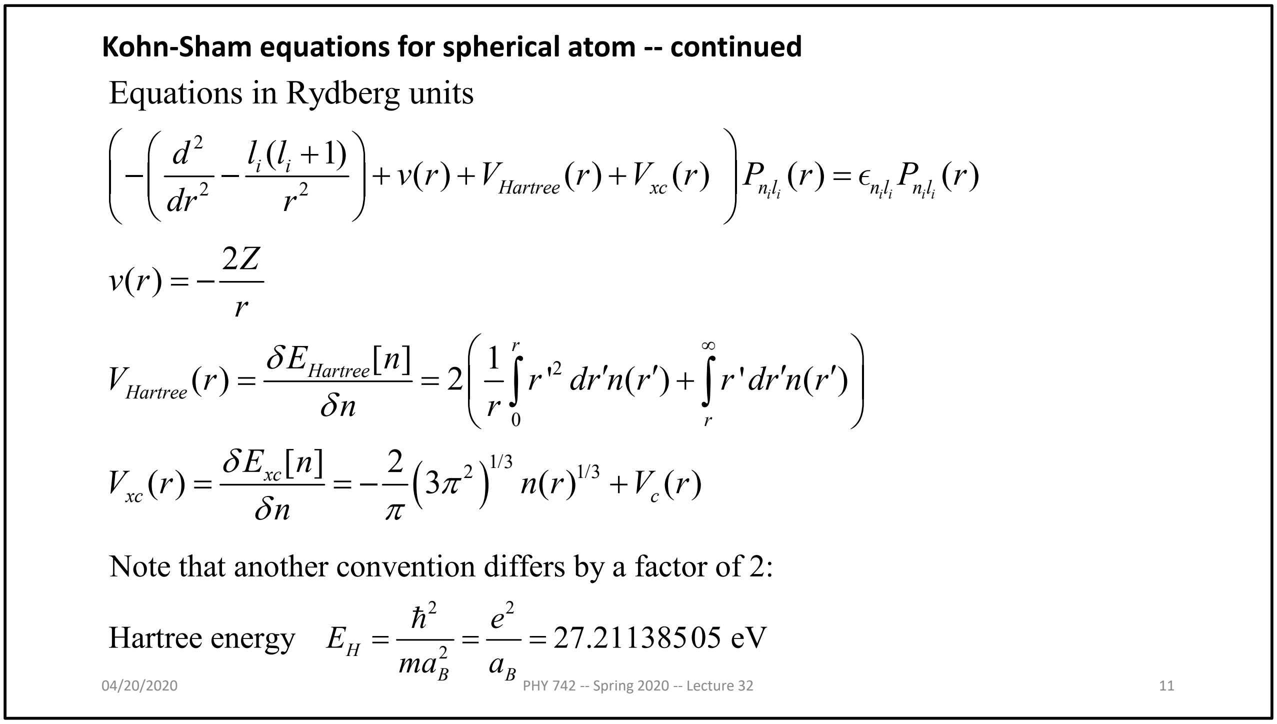
Convenient units:

Bohr radius $a_B = \frac{\hbar^2}{me^2}$

Rydberg energy $E_R = \frac{\hbar^2}{2ma_B^2} = \frac{e^2}{2a_B} = 13.60569253 \text{ eV}$

$r \leftarrow r/a_B \qquad \epsilon_{n_i l_i} \leftarrow \epsilon_{n_i l_i}/E_R$

Simplifying the differential equation and choosing convenient units.



## Kohn-Sham equations for spherical atom -- continued

Equations in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2}-\frac{l_i(l_i+1)}{r^2}\right)+v(r)+V_{Hartree}(r)+V_{xc}(r)\right)P_{n_il_i}(r)=\epsilon_{n_il_i}P_{n_il_i}(r)$$

$$v(r)=-\frac{2Z}{r}$$

$$V_{Hartree}(r)=\frac{\delta E_{Hartree}[n]}{\delta n}=2\left(\frac{1}{r}\int_0^r r'^2\,dr'n(r')+\int_r^\infty r'\,dr'n(r')\right)$$

$$V_{xc}(r)=\frac{\delta E_{xc}[n]}{\delta n}=-\frac{2}{\pi}\left(3\pi^2\right)^{1/3}n(r)^{1/3}+V_c(r)$$

Note that another convention differs by a factor of 2:

Hartree energy $E_H=\frac{\hbar^2}{ma_B^2}=\frac{e^2}{a_B}=27.21138505\text{ eV}$

Some detailed equations

## Kohn-Sham equations for spherical atom -- continued

Differential equations:

$$\left(-\left(\frac{d^2}{dr^2}-\frac{l_i(l_i+1)}{r^2}\right)+\underbrace{v(r)+V_{Hartree}(r)+V_{xc}(r)}_{V(r)}\right)P_{n_il_i}(r)=\epsilon_{n_il_i}P_{n_il_i}(r)$$

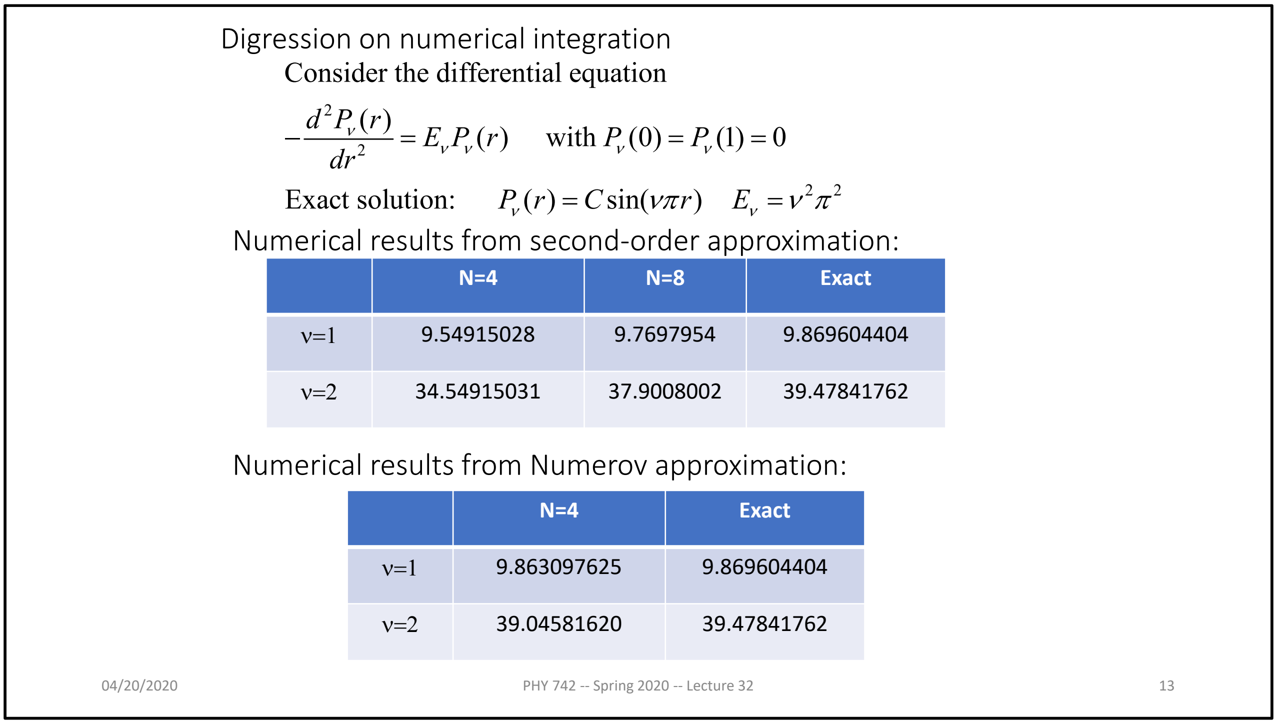
Boundary behaviors:

$$P_{n_il_i}(r)\xrightarrow[r=0]{}Cr^{l_i+1}$$

$$P_{n_il_i}(r)\xrightarrow[r=\infty]{}C'e^{-\sqrt{|\epsilon_{n_il_i}|}r}$$

**Notes on numerical integration of differential equations**

Please read numerov.pdf and then continue with this power point.



## Digression on numerical integration

Consider the differential equation

$$-\frac{d^2P_\nu(r)}{dr^2}=E_\nu P_\nu(r) \qquad \text{with } P_\nu(0)=P_\nu(1)=0$$

Exact solution: $P_\nu(r)=C\sin(\nu\pi r) \quad E_\nu=\nu^2\pi^2$

Numerical results from second-order approximation:

| | N=4 | N=8 | Exact |
|---|---|---|---|
| ν=1 | 9.54915028 | 9.7697954 | 9.869604404 |
| ν=2 | 34.54915031 | 37.9008002 | 39.47841762 |

Numerical results from Numerov approximation:

| | N=4 | Exact |
|---|---|---|
| ν=1 | 9.863097625 | 9.869604404 |
| ν=2 | 39.04581620 | 39.47841762 |

Some details about numerical integration

Some details:

Consider the differential equation

$$-\frac{d^2P_\nu(r)}{dr^2}=E_\nu P_\nu(r) \quad \text{with } P_\nu(0)=P_\nu(1)=0$$

Exact solution: $P_\nu(r)=C\sin(\nu\pi r) \quad E_\nu=\nu^2\pi^2$

$$-\frac{d^2P_\nu(r)}{dr^2}=E_\nu P_\nu(r)$$

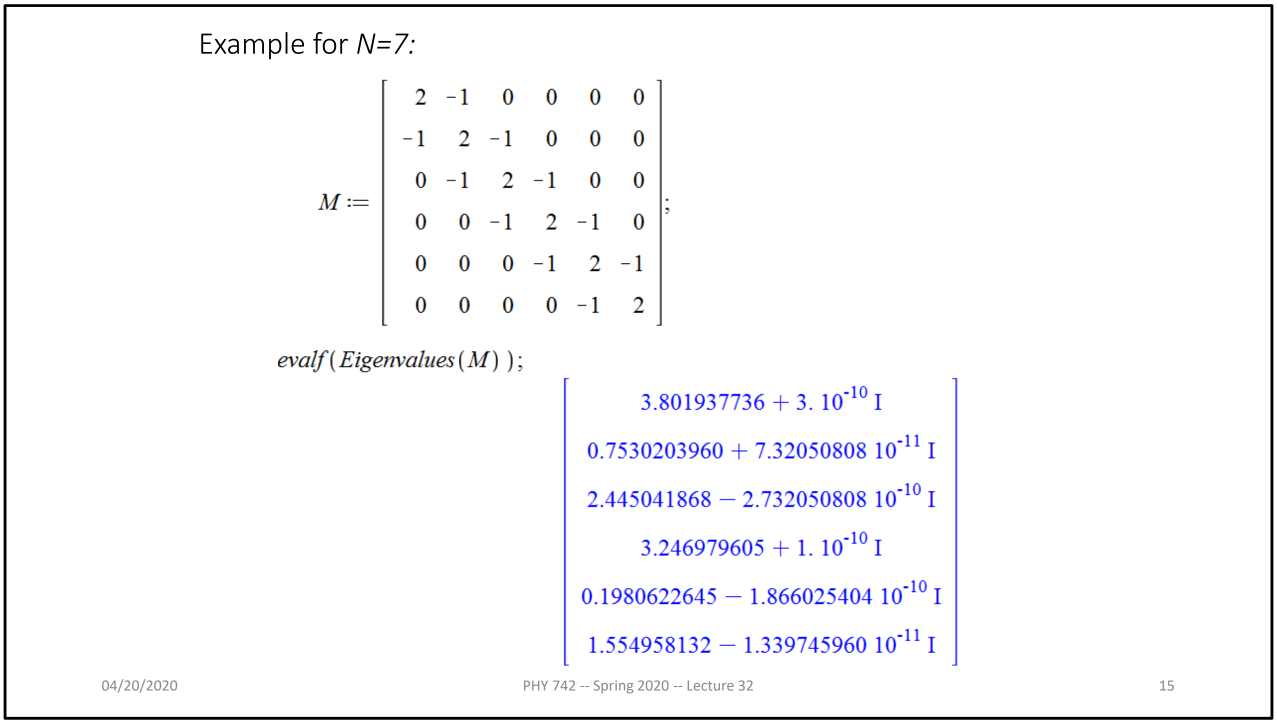
$$r\rightarrow r_n\equiv ns \quad \text{for } n=0,1,2...N \quad s=1/N$$

$$-\frac{d^2P_\nu(r_n)}{dr^2}\approx\frac{2P_\nu(r_n)-P_\nu(r_{n+1})-P_\nu(r_{n-1})}{s^2}$$

with $P_\nu(r_0)=\ P_\nu(r_N)=0$

Set up matrix problem for *(N-1)* unknown values;
$s^2E_\nu$ are matrix eigenvalues

Details of the setup



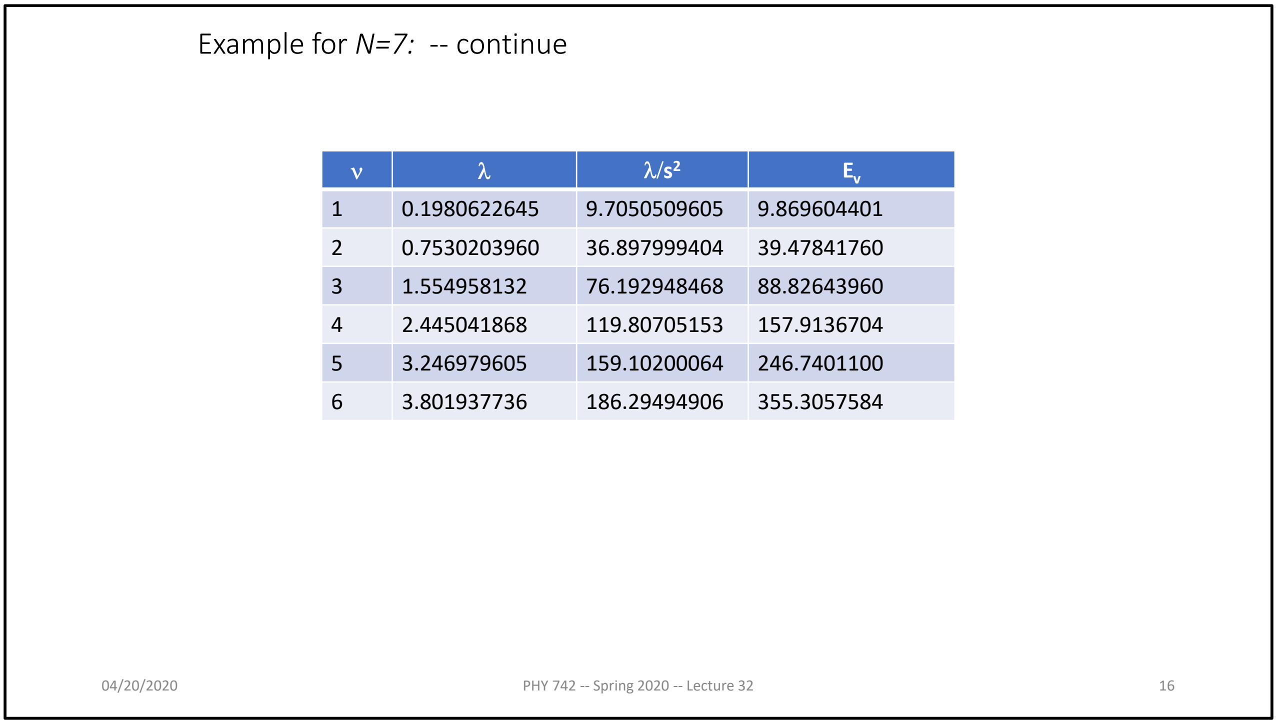
Example for *N=7:*

$$M := \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & -1 & 2 \end{bmatrix};$$

$$evalf(Eigenvalues(M));$$

$$\begin{bmatrix} 3.801937736 + 3.\ 10^{-10}\ \mathrm{I} \\ 0.7530203960 + 7.32050808\ 10^{-11}\ \mathrm{I} \\ 2.445041868 - 2.732050808\ 10^{-10}\ \mathrm{I} \\ 3.246979605 + 1.\ 10^{-10}\ \mathrm{I} \\ 0.1980622645 - 1.866025404\ 10^{-10}\ \mathrm{I} \\ 1.554958132 - 1.339745960\ 10^{-11}\ \mathrm{I} \end{bmatrix}$$

Results using Maple



Example for *N=7:* -- continue

| $\nu$ | $\lambda$ | $\lambda/s^2$ | $E_\nu$ |
|---|---|---|---|
| 1 | 0.1980622645 | 9.7050509605 | 9.869604401 |
| 2 | 0.7530203960 | 36.897999404 | 39.47841760 |
| 3 | 1.554958132 | 76.192948468 | 88.82643960 |
| 4 | 2.445041868 | 119.80705153 | 157.9136704 |
| 5 | 3.246979605 | 159.10200064 | 246.7401100 |
| 6 | 3.801937736 | 186.29494906 | 355.3057584 |

Summary. Notice that lowest eigenvalues are estimated the best.