Announcements:
- error in Act. #9, p.78 – should be \( \frac{-\hbar^2}{2m_e} \left( \nabla_1^2 + \nabla_1^2 \right) - ... \)
- Assignment #7 due next Monday

- Next few classes:
  - Wed. Linux exercises
  - Fri. beginning Gaussian03
  - Mon. Huckel (Act. #14/15)

- begin reading Cramer Ch. 4

Today:
- quick quiz
- recap of ME atoms
\[ E_{1e}(Z, n) = -\frac{1}{2} \left( \frac{m_e e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \right) \left( \frac{Z}{n} \right)^2 = -\frac{1}{2} E_h \left( \frac{Z}{n} \right)^2 = -(13.6 \text{ eV}) \left( \frac{Z}{n} \right)^2 \]

atomic unit of energy = \( E_h \)

**TABLE A.8** Wavefunctions for Hydrogen-like Atoms.

\[ \Psi_{1s} = \Psi_{100} = \frac{1}{\pi^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \]
\[ \Psi_{2s} = \Psi_{200} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \]
\[ \Psi_{2p_z} = \Psi_{2p_z} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a_0} \right)^{5/2} r e^{-Zr/2a_0} \cos \theta \]
Multi-Electron Atoms

1e atom:
\[ \hat{H} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} = \hat{h}(1) \]
\[ \Psi_{n,l,m_l}(r, \theta, \phi) = \Psi(1) \]

2e atom:
\[ \hat{H} = \left( -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} \right) + \left( -\frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} \right) + \frac{1}{r_{12}} \]
\[ \hat{h}(1) \quad \hat{h}(2) \quad V_{ee}(1,2) \]
\[ \Psi(\vec{r}_1, \vec{r}_2) = \Psi(1,2) \]

(in atomic units: \( m_e, 4\pi\varepsilon_0, \hbar, e = 1 \))

all coords. of \( e \neq 1 \)

even for only 2 \( e \), exact solutions are impossible due to \( V_{ee} \) term
Table 1.1 Useful quantities in atomic and other units

<table>
<thead>
<tr>
<th>Physical quantity (unit name)</th>
<th>Symbol</th>
<th>Value in a.u.</th>
<th>Value in SI units</th>
<th>Value(s) in other units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular momentum</td>
<td>ℏ</td>
<td>1</td>
<td>$1.055 \times 10^{-34}$ J s</td>
<td>$2.521 \times 10^{-35}$ cal s</td>
</tr>
<tr>
<td>Mass</td>
<td>m_e</td>
<td>1</td>
<td>$9.109 \times 10^{-31}$ kg</td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>e</td>
<td>1</td>
<td>$1.602 \times 10^{-19}$ C</td>
<td>$1.519 \times 10^{-14}$ statC</td>
</tr>
<tr>
<td>Vacuum permittivity</td>
<td>$4\pi\varepsilon_0$</td>
<td>1</td>
<td>$1.113 \times 10^{-10}$ C^2 J^{-1} m^{-1}</td>
<td>$2.660 \times 10^{-21}$ C^2 cal^{-1} Å^{-1}</td>
</tr>
<tr>
<td>Length (bohr)</td>
<td>a_0</td>
<td>1</td>
<td>$5.292 \times 10^{-11}$ m</td>
<td>$0.529$ Å</td>
</tr>
<tr>
<td>Energy (hartree)</td>
<td>E_h</td>
<td>1</td>
<td>$4.360 \times 10^{-18}$ J</td>
<td>$627.51$ kcal mol^{-1}</td>
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<tr>
<td>Electric dipole moment</td>
<td>e_0</td>
<td>1</td>
<td>$8.478 \times 10^{-30}$ C m</td>
<td></td>
</tr>
<tr>
<td>Electric polarizability</td>
<td>$\varepsilon_0^2 E_h^{-1}$</td>
<td>1</td>
<td>$1.649 \times 10^{-41}$ C^2 m^2 J^{-1}</td>
<td>$2.626 \times 10^3$ kJ mol^{-1}</td>
</tr>
<tr>
<td>Planck's constant</td>
<td>h</td>
<td>$2\pi$</td>
<td>$6.626 \times 10^{-34}$ J s</td>
<td>$27.211$ eV</td>
</tr>
<tr>
<td>Speed of light</td>
<td>c</td>
<td>$1.370 \times 10^2$</td>
<td>$2.998 \times 10^8$ m s^{-1}</td>
<td>$2.195 \times 10^5$ cm^{-1}</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>$\mu_B$</td>
<td>0.5</td>
<td>$9.274 \times 10^{-28}$ J T^{-1}</td>
<td>$2.542$ D</td>
</tr>
<tr>
<td>Nuclear magneton</td>
<td>$\mu_N$</td>
<td>$2.723 \times 10^{-4}$</td>
<td>$5.051 \times 10^{-27}$ J T^{-1}</td>
<td></td>
</tr>
</tbody>
</table>


ENERGY CONVERSION FACTORS

\[ E = h\nu = h\bar{\nu} = kT; \ E_m = LE \]

<table>
<thead>
<tr>
<th>wavenumber (\bar{\nu})</th>
<th>frequency (\nu)</th>
<th>energy (E)</th>
<th>molar energy (E_m)</th>
<th>temperature (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm^{-1}</td>
<td>MHz</td>
<td>aJ</td>
<td>eV</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>(\bar{\nu}: 1 \text{ cm}^{-1})</td>
<td>(\approx 1)</td>
<td>$2.997925 \times 10^4$</td>
<td>$1.986447 \times 10^{-5}$</td>
<td>$1.239842 \times 10^{-4}$</td>
</tr>
<tr>
<td>(\nu: 1 \text{ MHz})</td>
<td>(\approx 3.33564 \times 10^{-5})</td>
<td>$6.626076 \times 10^{-10}$</td>
<td>$4.135669 \times 10^{-9}$</td>
<td>$1.519830 \times 10^{-10}$</td>
</tr>
<tr>
<td>1 aJ</td>
<td>(\approx 50341.1)</td>
<td>$1.509189 \times 10^9$</td>
<td>$6.241506$</td>
<td>$0.2293710$</td>
</tr>
<tr>
<td>1 eV</td>
<td>(\approx 8065.54)</td>
<td>$2.417988 \times 10^8$</td>
<td>$0.1602177$</td>
<td>$1$</td>
</tr>
<tr>
<td>1 E_h</td>
<td>(\approx 219474.63)</td>
<td>$6.579684 \times 10^9$</td>
<td>$4.359748$</td>
<td>$27.2114$</td>
</tr>
<tr>
<td>(E_m: 1 \text{ kJ/mol})</td>
<td>(\approx 83.5935)</td>
<td>$2.506069 \times 10^6$</td>
<td>$1.660540 \times 10^{-3}$</td>
<td>$1.036427 \times 10^{-2}$</td>
</tr>
<tr>
<td>(E_m: 1 \text{ kcal/mol})</td>
<td>(\approx 349.755)</td>
<td>$1.048539 \times 10^7$</td>
<td>$6.947700 \times 10^{-3}$</td>
<td>$4.336411 \times 10^{-2}$</td>
</tr>
<tr>
<td>(T: 1 \text{ K})</td>
<td>(\approx 0.693509)</td>
<td>$2.08367 \times 10^4$</td>
<td>$1.380658 \times 10^{-5}$</td>
<td>$8.61738 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Examples of the use of this table: 1 aJ $\approx 50341$ cm$^{-1}$

The symbol $\approx$ should be read as meaning 'corresponds to' or 'is equivalent to'


3/13/2006

CHEM 408 - Sp06

L3 - 4
• exact & simple solutions in absence of $V_{ee}$ because

if $\hat{H}(1,2,...) = \hat{h}(1) + \hat{h}(2) + ...$ and $\hat{h}(\alpha) \phi_j(\alpha) = \varepsilon_{j}^{(\alpha)} \phi_j(\alpha)$ $\alpha = 1, 2, ...$

then $\hat{H}(1,2,...) \Psi_{ij...}(1,2,...) = E_{ij...} \Psi_{ij...}(1,2,...)$ where

$\Psi_{ij\cdots}(1,2,...) = \phi_i(1)\phi_j(2)\cdots$ and $E_{ij\cdots} = \varepsilon_i^{(1)} + \varepsilon_j^{(2)} + ...$

• neglecting $V_{ee}$, the approximate $\Psi$ of a 2e atom is simply:

$\Psi(1,2) \equiv \phi_{n_1,l_1,m_1}(r_1,\theta_1,\varphi_1)\phi_{n_2,l_2,m_2}(r_2,\theta_2,\varphi_2)$

$E \equiv \varepsilon_{n_1,l_1,m_1} + \varepsilon_{n_2,l_2,m_2}$

• for example, the ground state of He would be described by:

$\Psi(1,2) \equiv \phi_{1,0,0}(\vec{r}_1)\phi_{1,0,0}(\vec{r}_2)$

$= N \exp(-2r_1) \exp(-2r_2)$ $= \text{“1s(1)1s(2)”}$
• neglecting $V_{ee}$ find $E_{app} = -4$, versus $E_{exp} = -2.9$ (+38% error)

• this $E_{app}$ is exact energy of $\Psi$ of $\hat{H}_{app} = \hat{H} - V_{ee}$; a better estimate uses

$$E \cong <\hat{H}>_{app} = \int \Psi_{app}^* \hat{H} \Psi_{app} d\tau$$

• for $\Psi_{app}(1,2) = \phi_i(1)\phi_j(2)$ with $\hat{h}\phi_i = \varepsilon_i \phi_i$ it is easy to show

$$<\hat{H}>_{app} = \varepsilon_i + \varepsilon_j + <V_{ee}>$$

$$<V_{ee}>_{app} = \int \int \phi_i^*(1)\phi_j^*(2)V_{ee}(1,2)\phi_i(1)\phi_j(2)d\tau_1d\tau_2$$

• for the He atom with $\Psi_{app} = N \exp(-2r_1)\exp(-2r_2)$

$$<V_{ee}>_{app} = N^2 \int \int \int \int \int dx_1dy_1dz_1dx_2dy_2dz_2 e^{-4|r_1|}e^{-4|r_2|} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$
• the integral is messy but doable; the result is $<V_{\text{eff}}> = \frac{5}{4} \, \text{E}_\text{h}$.

• the energy estimated by this method is $E \approx -2.75 \, \text{E}_\text{h}$, much closer to the experimental value (-2.9 \, \text{E}_\text{h}).

• $<\hat{H}>_{\text{app}}$ is guaranteed to be greater than the true energy by

The Variational Theorem:

$$<\hat{H}>_{\text{app}} \equiv \frac{\int \Psi^*_\text{app} \hat{H} \Psi_{\text{app}} \, d\tau}{\int \Psi^*_\text{app} \Psi_{\text{app}} \, d\tau} \geq E_1$$

where $\hat{H}$ is the exact Hamiltonian, $E_1$ the exact ground state $E$, and $\Psi_{\text{app}}$ any (appropriate) $\Psi$

• the variational theorem provides the basis for virtually all electronic structure calculations
• the V.T. provides a way to obtain a closer estimate of the ground state energy of He atom \(\rightarrow\) vary \(\Psi_{app}\) and look for lower \(E\)

• one approach is to vary size of 1e orbitals:
  
  \[
  \text{exact He}^+ \quad 1s = n \exp(-2r) \quad (2 = Z)
  \]

  \[
  \text{better He approx.} \quad 1s' = n' \exp(-Z_{eff}r)
  \]

• varying \(Z_{eff}\) one finds minimum \(<\hat{H}>_{app}\) for \(Z_{eff} = 27/16\), with
  
  \[
  E_{app} = <\hat{H}>_{app} = -2.85 \ E_h \ (>2\% \ err)
  \]

• variational \(\Psi = 1s'(1)1s'(2)\) provides better description of true \(\Psi\), which is more diffuse than He\(^+\) \(\Psi\)
# He Atom Energies

<table>
<thead>
<tr>
<th></th>
<th>Energy</th>
<th>Error</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/ $E_h$</td>
<td>/ %</td>
<td>/ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$V_{ee}$ neglected</td>
<td>-4.0000</td>
<td>38%</td>
<td>+991</td>
</tr>
<tr>
<td>HF $Z = 2$</td>
<td>-2.7500</td>
<td>-5.3%</td>
<td>-139</td>
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<tr>
<td>HF $Z_{eff} = 27/16$</td>
<td>-2.8477</td>
<td>-1.9%</td>
<td>-50</td>
</tr>
<tr>
<td>&quot;HF limit&quot;*</td>
<td>-2.8616</td>
<td>-1.4%</td>
<td>-38</td>
</tr>
<tr>
<td>Hylleraas 2 param</td>
<td>-2.8922</td>
<td>-0.4%</td>
<td>-10</td>
</tr>
<tr>
<td>&quot;HF limit&quot;* + full CI</td>
<td>-2.9032</td>
<td>-0.01%</td>
<td>-0.3</td>
</tr>
<tr>
<td>Experiment</td>
<td>-2.9034</td>
<td></td>
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</table>

* - calculations with cc-pVTZ basis set ($n=55$)
• could do better than 2% error by adding more flexibility into description of orbitals, for example:

\[ \phi(r) = c_1 \exp(-Z_1 r) + c_2 \exp(-Z_2 r) + c_3 \exp(-Z_3 r) + ... \]

with \( c_1, c_2, c_3, ... , Z_1, Z_2, Z_3, ... \) variational parameters

• but there is a limit to the accuracy of the results obtain when \( \Psi \) is constrained by the orbital approximation:

\[ \Psi(1,2,...,n) = \phi_1(1)\phi_2(2)...\phi_n(n) \]

• even taken to the “Hartree-Fock limit” (where additional variation no longer lowers \( E \)), this type of \( \Psi \) is still inaccurate
## He Atom Energies

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy / $E_h$</th>
<th>Error / %</th>
<th>Error / kJ mol$^{-1}$</th>
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<td>-10</td>
</tr>
<tr>
<td>&quot;HF limit&quot;* + full CI</td>
<td>-2.9032</td>
<td>-0.01%</td>
<td>-0.3</td>
</tr>
<tr>
<td>Experiment</td>
<td>-2.9034</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - calculations with cc-pVTZ basis set ($n=55$)
• what’s missing is (dynamical) electron correlation: a dependence of the instantaneous position of one electron on the positions of the other electrons in the system

• interpretation of multi-electron $\Psi$:

$$P(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = |\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n)|^2 d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_n$$

is the probability of $e\neq 1$ being within $d\vec{r}_1$ of location $\vec{r}_1$ and $e\neq 2$ being within $d\vec{r}_2$ of $\vec{r}_2$... and $e\neq n$ being within $d\vec{r}_n$ of $\vec{r}_n$

• the orbital approximation

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \ldots \phi_n(\vec{r}_n)$$

implies $P(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = p_1(\vec{r}_1) p_2(\vec{r}_2) \ldots p_n(\vec{r}_n)$, i.e. that electron positions are uncorrelated
$P(\vec{r}_R, \vec{r}_T) \neq P_R(\vec{r}_R)P_T(\vec{r}_T)$
• Hylleraas (1928) proposed the function:

\[
\Psi(\vec{r}_1, \vec{r}_2) = Ne^{-\zeta} e^{-\zeta r} (1 + b |\vec{r}_1 - \vec{r}_2|)
\]

with \(\zeta \leftrightarrow Z_{\text{eff}}\) and \(b\) variational parameters

• minimum \(E\) for \(\zeta = 1.85, b=0.364\), with \(E_{\text{app}} = -2.89\ \text{E}_h (-.4\%\) error)

• the graphs at right show the relative prob. of finding \(e_2\) at a point along the x axis given that \(e_1\) is at the point (1,0,0).
He Atom Energies

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy / Eₚ</th>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

* - calculations with cc-pVTZ basis set (n=55)
Electron Spin & the Symmetry of $\Psi$

1. In addition to the 3 quantum numbers resulting from the 3 spatial coordinates, electrons posses a spin coordinate which implies one further quantum number. There are only two spin states available to an electron, specified by the quantum number $m_s$

$$m_s = +1/2 \quad \text{up} \quad \uparrow \quad \alpha$$
$$m_s = -1/2 \quad \text{down} \quad \downarrow \quad \beta$$

2. Electronic wavefunctions (space+spin) must be antisymmetric with respect to the exchange of any pair of electrons:

$$\Psi(1,2,3,...,n) = -\Psi(2,1,3) = -\Psi(3,2,1) = +\Psi(3,1,2)$$

This requirement gives rise to the “Pauli principle”, that no two electrons in an atom can reside in the same spin-orbital, i.e. share the same \( \{n, l, m_l, m_s\} \)
The Orbital Approximation

• Although quantitatively inaccurate, the orbital approximation is the conceptual basis for understanding atomic structure.

• The essential idea is to think of $\Psi$ of a multi-electron atom as the product of 1\textit{e} orbitals like the wavefunctions of the 1\textit{e} atom, but with orbital exponents adjusted to account for the average effects of “screening” = \textit{e}-\textit{e} repulsion:

$$\Psi(1,2,...,n) \cong \phi_{n_1,l_1,m_1}^{(Z_1)}(1)\phi_{n_2,l_2,m_2}^{(Z_2)}(2)...\phi_{n_n,l_n,m_n}^{(Z_n)}(n)$$

• the ground state of He in such a picture could be described as

$$\Psi(1,2) \cong \phi_{1s}^{(1.7)}(1)\phi_{1s}^{(1.7)}(2)$$

• but to go beyond He, two further ideas related to electron “spin” are required
• Incorporating $e$ spin means that electrons reside in “spin-orbitals”:

\[ \chi_i(1) = \phi_i(x_1, y_1, z_1) \times \begin{pmatrix} \alpha(\omega_1) \\ \beta(\omega_1) \end{pmatrix} \]

spin coordinate

<table>
<thead>
<tr>
<th>spin</th>
<th>spatial</th>
<th>spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital</td>
<td>orbital</td>
<td>function</td>
</tr>
</tbody>
</table>

• Various notations exist. For example, the combination of a 2s spatial orbital and $\beta$ spin function can be denoted:

\[ \chi(1) = \phi_{2s}(1) \beta(1) = \overline{\phi_{2s}}(1) \]

\[ = 2s(1) \beta(1) = 2s(1) \]

• $\Psi$ in the orbital approximation then a product of spin-orbitals

• Proper $\Psi$ symmetry is most easily achieved using the Slater determinant.
Slater Determinant:

\[ \Psi(1,2,3...,N) = \frac{1}{N!} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \chi_3(1) & \ldots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \chi_3(2) & \ldots & \chi_N(2) \\ \chi_1(3) & \chi_2(3) & \chi_3(3) & \ldots & \chi_N(3) \\ \vdots & \vdots & \vdots & \ldots & \vdots \\ \chi_1(N) & \chi_2(N) & \chi_3(N) & \ldots & \chi_N(N) \end{vmatrix} \]

\( = \chi_1 \chi_2 \chi_3 \ldots \chi_N \)

- for example, for a 3e system:

\[ \Psi(1,2,3) = \frac{1}{3!} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \chi_3(1) \\ \chi_1(2) & \chi_2(2) & \chi_3(2) \\ \chi_1(3) & \chi_2(3) & \chi_3(3) \end{vmatrix} \]

\[ = \frac{1}{6} \{ \chi_1(1) \chi_2(2) \chi_3(3) + \chi_2(1) \chi_3(2) \chi_1(3) + \chi_3(1) \chi_1(2) \chi_2(3) \\
- \chi_3(1) \chi_2(2) \chi_3(3) - \chi_1(1) \chi_3(2) \chi_2(3) - \chi_2(1) \chi_1(2) \chi_3(3) \} \]

- such determinants are identically zero unless all the \( \chi_i \) are unique, thus the origin of the Pauli principle
• the ground-state structures of multi-\( e \) atoms are constructed by sequentially filling up 1\( e \) spin-orbitals whose spatial parts resemble H-atom orbitals with effective exponents

• the exponents and orbital energies depend on \( Z \) and on the electronic configuration; rationalize via screening:

\[
Z_{\text{eff}} = Z - \sigma(n, l)
\]

screening constant

• because of differential penetration to nucleus, for a given \( n \) (shell), screening varies as:

\[
\sigma(f) > \sigma(d) > \sigma(p) > \sigma(s)
\]

\[
E(f) > E(d) > E(p) > E(s)
\]

Atkins 3.21, 3.16
Fig. 2.19 Relative orbital energies of the elements hydrogen to sodium. Solid lines indicate one-electron orbital energies. Dashed lines represent experimental ionization energies which differ as a result of electron–electron interactions.


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Atomic-orbital energies as a function of atomic number for neutral atoms, as dated by Latter. [Figure redrawn by M. Kasha from R. Latter, *Phys. Rev.*, 99, 510 (1955).] Note the logarithmic scales. $E_i$ is the ground-state hydrogen-atom energy, $-13.6 \text{ eV}$.

$E_i \propto Z^2$

from: Levine, Quantum Chemistry, 5th Ed. (Prentice-Hall, 2000)
As (Z=33) from http://www.webelements.com/webelements

- Ground state electron configuration: \([\text{Ar}].3d^{10}.4s^2.4p^3\)
- Shell structure: 2.8.18.5
- Term symbol: \(^4S_{3/2}\)
# The Periodic Table

<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Li, Be</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Na, Mg</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>K, Ca</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Rb, Sr</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Cs, Ba, Lanthanoids, Actinoids</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>Fr, Ra, 57 La, 58 Ce, 59 Pr, 60 Nd, 61 Pm, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tm, 70 Yb, 89 Ac, 90 Th, 91 Pa, 92 U, 93 Np, 94 Pu, 95 Am, 96 Cm, 97 Bk, 98 Cf, 99 Es, 100 Fm, 101 Md, 102 No</td>
</tr>
</tbody>
</table>

Electron Distributions in Ar

Ar Radial Distributions

\[ P(r) = \frac{1}{r^2} \int |\psi(r)|^2 \, \frac{d^2r}{r^2} \]

HF total

3s Radial Distributions

\[ P(r) = \frac{1}{r^2} \int |\psi(r)|^2 \, \frac{d^2r}{r^2} \]

HF

1e

Z_{eff} = 11

\[ r / \xi \]

n=1

n=2

n=3

3s

3p

total

r / a

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from: Levine, Quantum Chemistry, 5th Ed. (Prentice-Hall, 2000)

**X-ray Diffraction**

![Graph](image)

**FIGURE 11.1** Radial distribution function in Ar as a function of $r$. The broken line is the result of a Hartree–Fock calculation. The solid line is the result of electron-diffraction data. [From L. S. Bartell and L. O. Brockway, *Phys. Rev.*, **90**, 833 (1953). Used by permission.]