Schrödinger equation:
- Operator form $\mathcal{H} \Psi = E \Psi$:
  - $\mathcal{H} = \hbar^2/8\pi^2m \nabla^2 + V$
  - The Hamilton operator perform an operation (total energy expression = kinetic (Laplacian) + potential) on the function (e.g.: electron orbital) that follows it.
  - If the result is constant times the function itself then the function is called eigenfunction (molecular orbitals as set of atomic orbitals) and the constant is eigenvalue (orbital energy).

One-electron atoms:
- $V = -Ze^2/r$ - set the origin of the Cartesian space at the center of the nucleus $\Psi(x, y, z)$ can be converted to $\Psi(r, \theta, \phi)$ in polar coordinates $= R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$ ⇒ separates into radial and angular functions
- To satisfy boundary conditions – certain constants needs to be introduced ⇒ quantum numbers
  - $n = 1, 2, 3, \ldots$ (K, L, M, \ldots) approximate energy and size of the wavefunction
  - $l = 0, 1, 2, \ldots$ (s, p, d, \ldots) absolute value of the angular momentum
  - $m_l = -l, \ldots, 0, \ldots l$ real angular momentum (vectors with sign)
  - $\Psi_{n,l,m_l}$ defines a solution commonly called orbital described by $= R_{n,l}(r) \cdot \Theta_{l,m}(\theta) \cdot \Phi_{m}(\phi)$

- Radial Function $R(r)$
  - The orbital size increases as $n$ increases, maximums at $n^2 \cdot a_0$ (average distance over time: 1s at 70 pm, 2s at 300 pm, 3s 650 pm)
  - s-type orbitals have infinite density at the nucleus (Mössbauer spectroscopy) - exponential decay to zero at large distances
  - Radial nodes $(n-1-l)$ define the zero probability of finding electrons at a certain position

- Angular Functions $\Theta(\theta), \Phi(\phi)$
  - Define the shape and sign of the atomic orbitals with quantum numbers
  - Angular nodes $(l)$ define the zero probability of finding electrons in a certain plane
  - Linear combination of the orbitals

Polyelectronic atoms:
- Experiment: H atom in a magnetic field ⇒ the number of spectral lines increases
- Stern and Gerlach: Ag atoms in a magnetic field split into two beams ⇒ interpretation of Ag atomic spectra show no angular momentum $(l=0)$ for the highest electron $(5s^1)$
- Uhlenbeck and Goudsmit: interpretation with spin angular momentum $S = \frac{1}{2}$ ⇒ parallel and antiparallel alignment with the magnetic field ⇒ spin quantum number $m_s = \pm \frac{1}{2}$.
- Pauli: exclusion principle requires unique $n, l, m_l, m_s$ quantum numbers for each electron (in quantum chemistry: antisymmetry ⇒ $\Psi$ changes sign if the coordinates of electrons are changed)
- Hund: rules based on pure electrostatic considerations
  - $1^{st}$: it takes energy to bring electrons closer together – antiparallel and parallel spins within the same $l$ are degenerate in classical treatment ⇒ take the square of the wavefunction in quantum theory and the antiparallel is closer to each other, (max $S$) ⇒ exchange stabilization
  - $2^{nd}$: the electrons stay as far apart as possible ⇒ most stable is the largest angular momentum (max. $L$) with everything else the same ⇒ electron repulsion due to correlation
  - $3^{rd}$: orbital $(L)$ and spin moments $(S)$ can couple (give total angular momentum, $J$); antiparallel for electrons $< 2l +1$ (half occupied orbital) and parallel for others ⇒ magnetism
- Orbital penetration: lifts the degeneracy of orbitals with same $n$ due to outer orbital’s probability at distances more typical for inner orbitals with lower principal numbers in the order of $s > p > d$
- Experiment: atomic spectral lines of alkali metals, terms are more separated than for the H
Building up atoms: "aufbau" process

- start with the lowest available empty orbital in the order of n+l with smaller n first (3p vs. 4s) and fill each orbital up before start pairing up electrons

1. H – 1s\(^1\) ⇒ 1\(^2\)S\(_{1/2}\)
2. He – 1s\(^2\) ⇒ 1\(^1\)S\(_0\)
3. Li – 1s\(^2\) 2s\(^1\) ⇒ 2\(^2\)S\(_{1/2}\)
4. Be – 1s\(^2\) 2s\(^2\) or 1s\(^2\) 2s\(^1\) 2p\(^1\) ⇒ 2s more penetrating than 2p, i.e. lower in energy ⇒ 2 \(^1\)S\(_0\)
5. B – 1s\(^2\) 2s\(^2\) 2p\(^1\) ⇒ \(n = 2; l = 1; m_l = \pm 1, 0; m_s = \pm \frac{1}{2}\) ⇒ orbital momentum and electron spin vector coupling introduces 'j' inner quantum number, \(j = m_l + m_s\)

<table>
<thead>
<tr>
<th>B</th>
<th>1s(^2)</th>
<th>2s(^2)</th>
<th>2p(^1)</th>
</tr>
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<tbody>
<tr>
<td>n</td>
<td>1</td>
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<td>2</td>
</tr>
<tr>
<td>m(_l)</td>
<td>0</td>
<td>0</td>
<td>-1,0,1</td>
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<tr>
<td>m(_s)</td>
<td>(\frac{1}{2},-\frac{1}{2})</td>
<td>(\frac{1}{2},-\frac{1}{2})</td>
<td>(\frac{1}{2},-\frac{1}{2})</td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0</td>
<td>±(\frac{1}{2})</td>
</tr>
<tr>
<td>j</td>
<td>0</td>
<td>0</td>
<td>±(\frac{3}{2}, \frac{1}{2}), ±(\frac{1}{2})</td>
</tr>
</tbody>
</table>

```
⇒ 2 \(^2\)P
⇒ 2 \(^2\)P\(_{3/2}\) or 2 \(^2\)P\(_{1/2}\)
```

experiment: in a magnetic field a state can split into \(2J+1\), \(J = L(M_l)+S(M_s)\) states (Zeeman effect)

6. C – 1s\(^2\) 2s\(^2\) 2p\(^2\) ⇒ \(n = 2; l = 1; m_l = \pm 1, 0; m_s = \pm \frac{1}{2}\) ⇒ throw out all the doubly occupied orbitals since \(L\) and \(S\) will be zero and final term is \(^1\)S\(_0\)

<table>
<thead>
<tr>
<th>C</th>
<th>2p(_x)^{1}\</th>
<th>2p(_y)^{1}\</th>
<th>2p(_z)^{0}\</th>
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<td>2</td>
<td>2</td>
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<tr>
<td>m(_l)</td>
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<td>0</td>
<td>1</td>
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<tr>
<td>m(_s)</td>
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<td>(\frac{1}{2},-\frac{1}{2})</td>
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<tr>
<td>s</td>
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<td>(\frac{1}{2},-\frac{1}{2})</td>
<td>(\frac{1}{2},-\frac{1}{2})</td>
</tr>
<tr>
<td>j</td>
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<td>(\frac{1}{2},-\frac{1}{2})</td>
<td>(\frac{3}{2}, \frac{1}{2})</td>
</tr>
</tbody>
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