UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

# Approximation Methods

# Time Independent Perturbation Theory

- We have already seen, in the spin-orbit case, that in some instances it is necessary to consider a perturbation of the system...

- In particular, let's consider a system described by the Hamiltonian $H_0$ and assume that we have solved the S.E. for that system, finding eigenvectors and eigenvalues (indeed, this was the case of the Hydrogen atom involved in the spin-orbit analysis, for instance)

$$\hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0 \qquad \text{with} \quad \langle \psi_m^0 | \psi_n^0 \rangle = \delta_{n,m}$$

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$$\hat{H}_0 \Psi_n^0 = E_n^0 \Psi_n^0 \qquad \text{with} \quad \langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{n,m}$$

- If we consider now a weak perturbation, we can write

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

and the eigenvector equation:

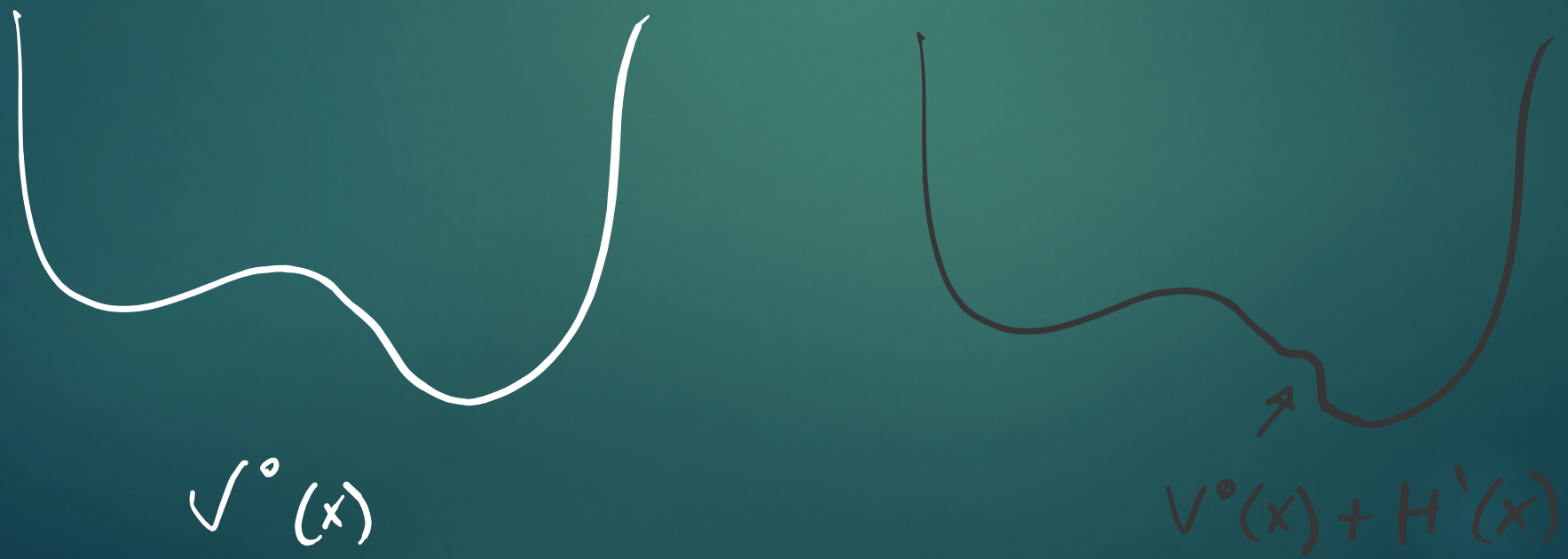
$$\hat{H} \Psi_n = E_n \Psi_n = \left(\hat{H}_0 + \hat{H}'\right) \Psi_n$$

# Time Independent Perturbation Theory

$$\hat{H}\Psi_n = E_n \Psi_n = \left(\hat{H}_0 + \hat{H}'\right)\Psi_n$$

In general, this equation will not have exact analytic solutions, but we can find approximate solutions by the so called "perturbation theory".

But what does it mean "weak perturbation"?

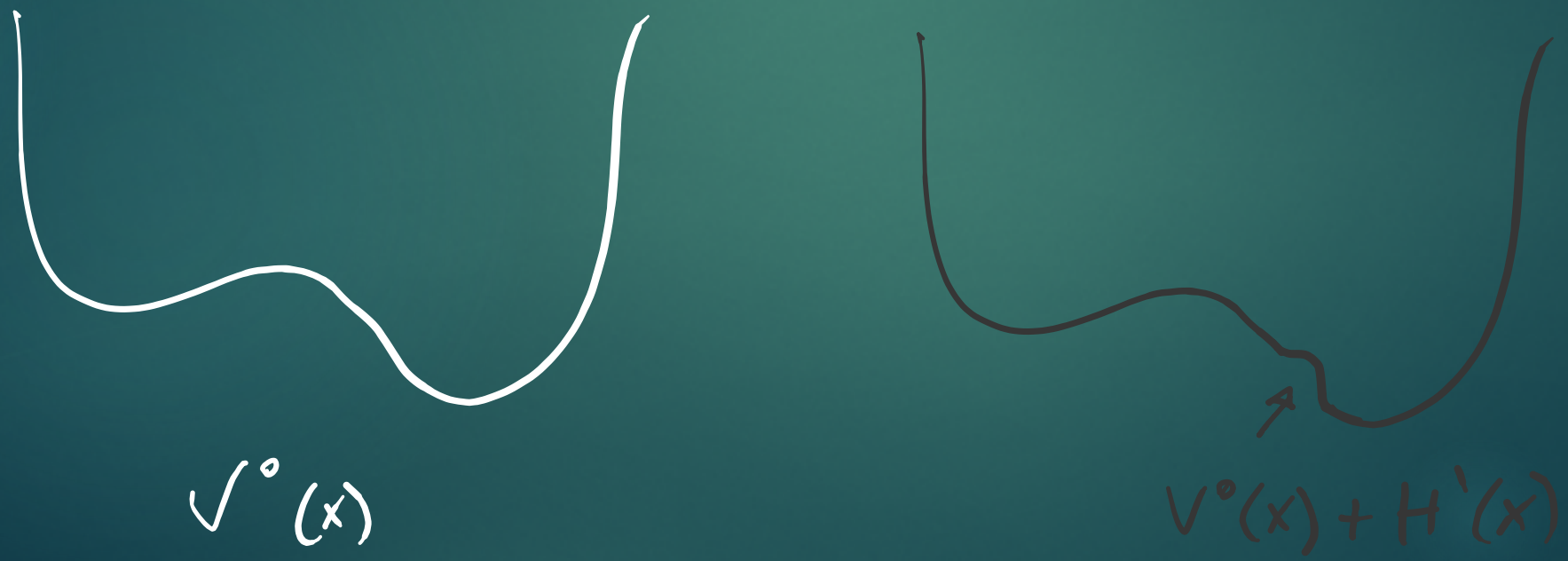


# Time Independent Perturbation Theory

$$\hat{H}\Psi_n = E_n\Psi_n = \left(\hat{H}_0 + \hat{H}'\right)\Psi_n$$

But what does it mean "weak perturbation"?

Classically, it would mean that the variation in energy of the system, due to the perturbation, is small.



# Time Independent Perturbation Theory

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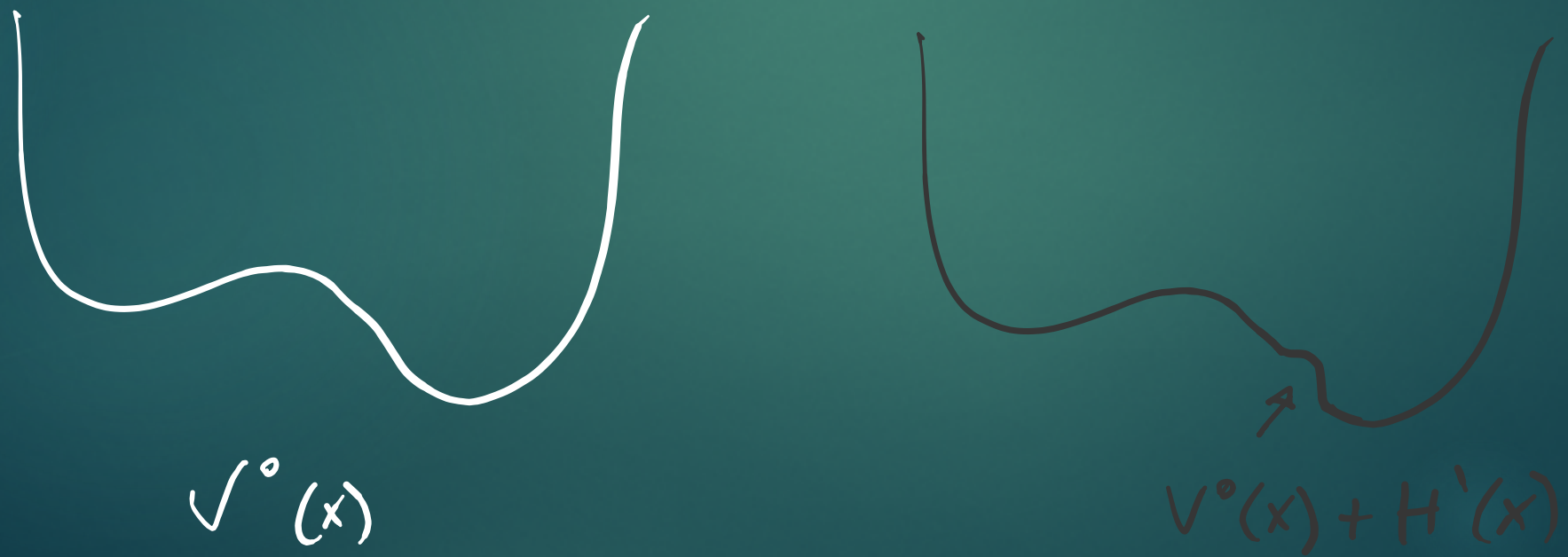
But what does it mean "weak perturbation"?

In quantum mechanics, it is more meaningful to state that the expectation values of H' must be much smaller than that of H°



# Time Independent Perturbation Theory

$$\hat{H}\,\Psi_n = E_n\,\Psi_n = \left(\hat{H}_0 + \hat{H}'\right)\Psi_n$$

If we have a weak perturbation, I can write:

$$H' = \lambda H'' \quad \text{with} \quad \lambda << 1$$

$$H'' = \frac{H'}{\lambda} \simeq H^0$$

Thus: $\hat{H} = \hat{H}^0 + \hat{H}' = \hat{H}^0 + \lambda \hat{H}''$

Still $\hat{H}^0\,\Psi_n^0 = E_n^0\,\Psi_n^0$

with $E_n^0$ and $\Psi_n^0$ that are known

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# Time Independent Perturbation Theory

$$\hat{H}\Psi_n = E_n \Psi_n = \left(\hat{H}_0 + \hat{H}'\right)\Psi_n$$

If we have a weak perturbation, I can write:

$$\hat{H} = \hat{H}^0 + \lambda H''$$

I can expand $E_n$ and $\Psi_n$ by power series in $\lambda$, and when $\lambda \to 0$ their values will be the unperturbed ones.

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)}$$

$E_n^{(1)}$, $\Psi_n^{(1)}$ are first order corrections

$E_n^{(2)}$, $\Psi_n^{(2)}$ " second order corrections

Thus $\left(\hat{H}^0 + \lambda \hat{H}''\right)\left(\Psi_n^0 + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots\right) = \left(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\right)\left(\Psi_n^0 + \lambda \Psi_n^{(1)} + \dots\right)$

# Time Independent Perturbation Theory

$$\left(\hat{H}^0 + \lambda \hat{H}^{1}\right)\left(\psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} \dots\right) = \left(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\right)\left(\psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots\right)$$

By collecting like powers of $\lambda$ , I can write:

$$\hat{H}^0 \psi_n^0 + \lambda\left(\hat{H}^0 \psi_n^{(1)} + \hat{H}^{1} \psi_n^0\right) + \lambda^2\left(\hat{H}^0 \psi_n^{(2)} + \hat{H}^{1} \psi_n^{1}\right) + \dots$$

$$= E_n^0 \psi_n^0 + \lambda\left(E_n^0 \psi_n^{(1)} + E_n^{(1)} \psi_n^0\right) + \lambda^2\left(E_n^0 \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^0\right) + \dots$$

# Time Independent Perturbation Theory

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$$= E_n^0 \psi_n^0 + \lambda\left(E_n^0 \psi_n^{(1)} + E_n^{(1)} \psi_n^0\right) + \lambda^2\left(E_n^0 \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^0\right) + \dots$$

This is satisfied if all terms with same power order are equal:

$$H^0 \psi_n = E_n^0 \psi_n^0 \quad \rightarrow \text{with } \lambda^0$$

$$H^0 \psi_n^{(1)} + H^{(1)} \psi_n^0 = E_n^0 \psi_n^{(1)} + E_n^{(1)} \psi_n^0 \quad \rightarrow \text{ u } \lambda^1$$

$$H^0 \psi_n^{(2)} + H^{(1)} \psi_n^1 = E_n^0 \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^0 \quad \rightarrow \text{ u } \lambda^2$$

...

# Time Independent Perturbation Theory

First order in $\lambda$

$$H^0 \psi_n^{(1)} + H' \psi_n^0 = E_n^0 \psi_n^{(1)} + E_n^{(1)} \psi_n^0 \longrightarrow \text{multiplying by } \psi_n^0$$

$$\langle \psi_n^0 | H^0 | \psi_n^{(1)} \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n^0 | E_n^0 | \psi_n^{(1)} \rangle + \langle \psi_n^0 | E_n^{(1)} | \psi_n^0 \rangle$$

$$\Rightarrow E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle + E_n^{(1)} \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{1}$$

$$\Rightarrow E_n^{(1)} = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

# Time Independent Perturbation Theory

First order in $\lambda$

$$E_n^{(1)} = \langle \psi_n^0 | H'' | \psi_n^0 \rangle$$

Because $\hat{H} = \hat{H}^0 + \hat{H}' = \hat{H}^0 + \lambda \hat{H}''$ and $\left(\hat{H}^0 + \lambda \hat{H}''\right) \psi_n = \left(E_n^0 + \lambda E_n^{(1)}\right) \psi_n$

($\hat{H}$ : $E_n$)

$$E_n = E_n^0 + \lambda E_n^{(1)} = E_n^0 + \lambda \langle \psi_n^0 | H'' | \psi_n^0 \rangle$$

$$\Rightarrow E_n = E_n^0 + \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

↓ the first order correction is $\langle H' \rangle$
the expectation value of $H'$

# Time Independent Perturbation Theory

First order correction:

$$E_n = E_n^0 + \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle$$

One can also calculate the correction to the eigenstate:

$$\psi_n = \psi_n^0 + \sum_{j \neq n} \frac{\langle \psi_j^0 | \hat{H}' | \psi_n^0 \rangle}{E_n^0 - E_j^0} | \psi_j^0 \rangle$$

Notice that j are the states different than the perturbed one, thus in case of perturbation, the wavefunction is affected also by the unperturbed states close to n.

# Time Independent Perturbation Theory

First order correction:

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Notice also that in case of degeneracy, different states have the same eigenvalue, thus the denominator in the summation makes no sense, in such a case! We would need the degenerate perturbation theory...

# Time Independent Perturbation Theory

First order correction:

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One can also calculate the correction to the eigenstate:

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One can also calculate the second order correction:

$$E_n = E_n^0 + \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle + \sum_{j \neq n} \frac{|\langle \psi_j^0 | \hat{H}' | \psi_n^0 \rangle|^2}{E_n^0 - E_j^0}$$

# Time Independent Perturbation Theory

Let's apply the perturbation theory to find the s.o. correction to the energy levels of Hydrogen:

$$H_{SO} = \frac{e}{m_e}\,\vec{S}\cdot\vec{B} = \frac{e^2}{4\pi\varepsilon_0}\,\frac{1}{m_e^2 c^2 r^3}\,\vec{S}\cdot\vec{L}$$

↓

spin-orbit interaction

But

$$\vec{J}^2 = (\vec{L}+\vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S} \quad \Rightarrow \quad \vec{L}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

Thus $H_{SO}\,\psi = f(r)\,\vec{S}\cdot\vec{L}\,\psi = \frac{1}{2}\left[J^2\psi - L^2\psi - S^2\psi\right] = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\psi$

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One can calculate

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)\,n^3 a^3}$$

Thus:

$$E_{so}^{1} = \langle \psi_n^0 | H_{so} | \psi_n^0 \rangle = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2}\,\frac{(\hbar^2/2)\left[j(j+1) - l(l+1) - s(s+1)\right]}{l\left(l+\frac{1}{2}\right)(l+1)\,n^3 a^3}$$

# Time Independent Perturbation Theory

Thus: $E^1_{s_0} = \langle \psi^0_n | H_{s_0} | \psi^0_n \rangle = \dfrac{e^2 (\hbar^2/2)\left[j(j+1) - l(l+1) - s(s+1)\right]}{8\pi\varepsilon_0 m^2 c^2 \, l\left(l+\frac{1}{2}\right)(l+1) n^3 a^3}$

but: $E_1 = -\dfrac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = -\dfrac{e^2}{8\pi\epsilon_0 a} = -13.6 \text{ eV}$ and $E^0_n = \dfrac{E_1}{n^2}$

Introducing $\alpha = \dfrac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \dfrac{1}{137}$

$$E^1_{s_0} = -\frac{E^0_n \alpha^2 \left[j(j+1) - l(l+1) - s(s+1)\right]}{2n\, l\left(l+\frac{1}{2}\right)(l+1)}$$

# Time Independent Perturbation Theory

$$E^1_{s0} = -\frac{E^0_n \alpha^2 \left[j(j+1) - l(l+1) - s(s+1)\right]}{2n l\left(l+\frac{1}{2}\right)(l+1)}$$

→ Note that degeneracy in $l$ disappears.

Together with the relativistic correction (not seen here) I obtain the new energy levels for H:

$$E_{n,j} = -\frac{13.6\ eV}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

Term due to the "fine structure" of H

# Time Independent Perturbation Theory

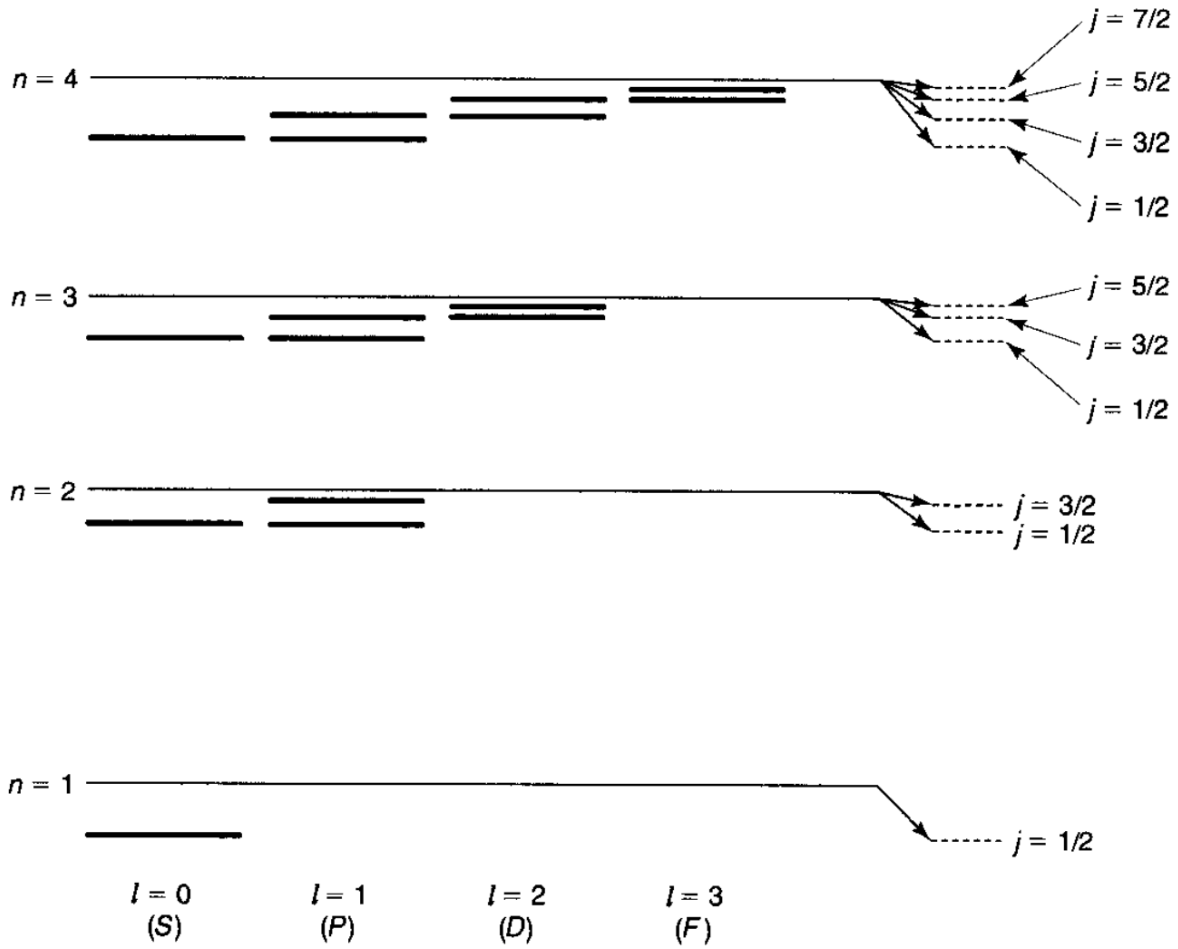
$$E_{n,j} = -\frac{13.6\,eV}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right]$$

Notice that for $n=1$

$l=0 \quad m=0 \quad m_s=\frac{1}{2} \quad j=\frac{1}{2}$

$$E^{(1)}_{F.S.} = -13{,}6\,eV \cdot \alpha^2 \times \frac{1}{4} = -0.18\,meV$$

Without the term of the fine structure, the energy was higher!




Energy levels of hydrogen, including fine structure (not to scale).

# The Variational Principle

**Theorem:**

If $\hat{H}$ is a Hamiltonian operator, and $E_g$ (the ground state energy) is its minimum eigenvalue, then:

$$E_g \leq \langle \Psi | \hat{H} | \Psi \rangle , \qquad \forall |\Psi\rangle \;|\; \langle \Psi | \Psi \rangle = 1$$

This is not obvious, because the wavefunction here is not an eigenstate of the operator, but a general vector of the Hilbert vector space.

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**Demonstration:**

$\Psi = \sum_n c_n \Psi_n$ where $\Psi_n$ are eigenfunction of $\hat{H}$, thus $\hat{H}\Psi_n = \hat{E}\Psi_n$

starting from $\langle \Psi | \Psi \rangle = 1$ we can write:

$$\langle \Psi | \Psi \rangle = 1 = \left\langle \sum_m c_m \Psi_m \middle| \sum_n c_n \Psi_n \right\rangle = \sum_{m,n} c_m^* c_n \langle \Psi_m | \Psi_n \rangle = \sum_n |c_n|^2$$

# The Variational Principle

$$\langle\Psi|\Psi\rangle = 1 = \left\langle \sum_n c_n \Psi_n \middle| \sum_n c_n \Psi_n \right\rangle = \sum_{m,n} c_m^* c_n \langle \Psi_m | \Psi_n \rangle = \sum_n |c_n|^2$$

Also:

$$\langle\Psi|H|\Psi\rangle = \left\langle \sum_n c_n \Psi_n \middle| H \sum_n c_n \Psi_n \right\rangle = \sum_{m,n} c_m^* E_n c_n \langle \Psi_m | \Psi_n \rangle = \sum_n E_n |c_n|^2$$

But $E_g \leq E_n \Rightarrow \sum_n E_n |c_n|^2 \geq E_g \sum_n |c_n|^2 = E_g$

Thus $\langle\Psi|H|\Psi\rangle \geq E_g$ Q.E.D.

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The variational principle is very useful in many applications where the exact solutions of the S.E. cannot be found analytically. But, if we have hypotheses for a general formulation of the solutions (e.g. it is an exponential function, or it is a gaussian function, or it is ...), then we can optimize the parameters of the "trial" solution, by minimizing the expectation value of the Hamiltonian.

# Multiple particle systems

The Hamiltonian of a multi-particle system can be written in general as:

$$H(x_1, x_2, \dots, x_N, t) = \sum_{i=1,N} \frac{p_i^2}{2\, m_i} + V(x_1, x_2, \dots, x_N, t)$$

Suppose that the particles do not interact with one another. This implies that each particle moves in a common potential:

$V(x_1, x_2, \dots, x_N, t) = \sum_{i=1,N} V(x_i, t)$ and hence $H(x_1, x_2, \dots, x_N, t) = \sum_{i=1,N} H_i(x_i, t)$

In other words, for the case of non-interacting particles, the multi-particle Hamiltonian of the system can be written as the sum of $N$ independent single-particle Hamiltonians. Then, the multi-particle wavefunction can be written as the product of N independent single-particle wavefunctions:

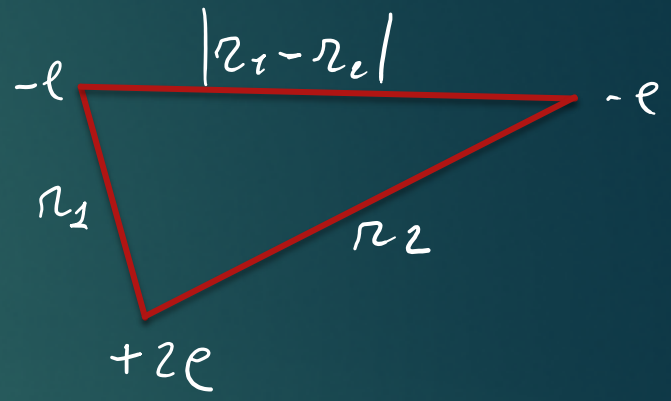
$$\psi(x_1, x_2, \dots, x_N, t) = \psi_1(x_1, t)\, \psi_2(x_2, t) \dots \psi_N(x_N, t)$$

# Helium atom

- A helium atom consists of a nucleus of charge +2e surrounded by two electrons.
- The Hamiltonian of the system thus takes the form:

$$H = -\frac{\hbar^2}{2\,m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

(2 and 2: atomic number)




The five terms in the Hamiltonian represent, respectively, the kinetic energies of electrons 1 and 2, the nuclear attractions of electrons 1 and 2, and the repulsive interaction between the two electrons. It is this last contribution which prevents an exact solution of the Schrödinger equation.

In seeking an approximation to the ground state, we might first work out the solution in the absence of this last term...

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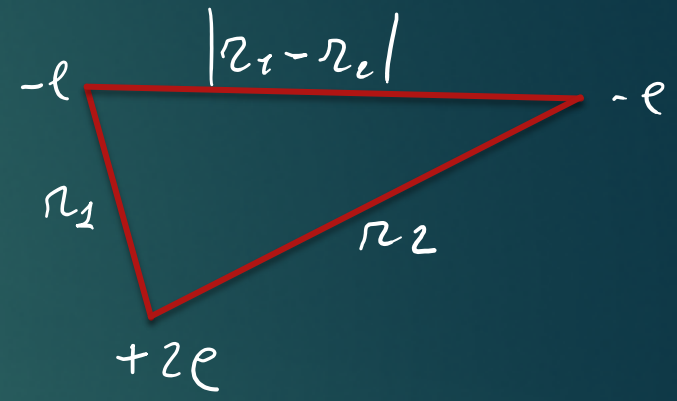
$$\Psi_0(r_1, r_2) = \psi_{1s}(r_1)\,\psi_{1s}(r_2) =$$

$$= \psi_{100}(r_1)\,\psi_{100}(r_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$




The energy will be $2 \cdot (Z^2) E_1 = 2\,(4)\,E_1 = 8E_1 \simeq -109\,eV$

The experimental energy is $E_g \simeq -79\,eV$

not a good approximation obviously neglecting e-e interaction.

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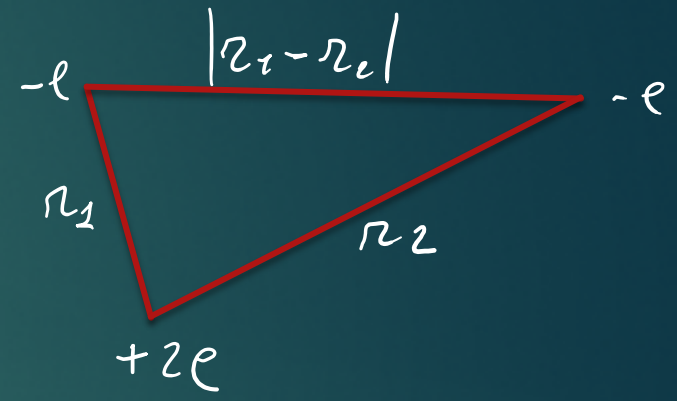


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$$E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \simeq -13{,}6\ eV$$

↳ Ground state of Hydrogen

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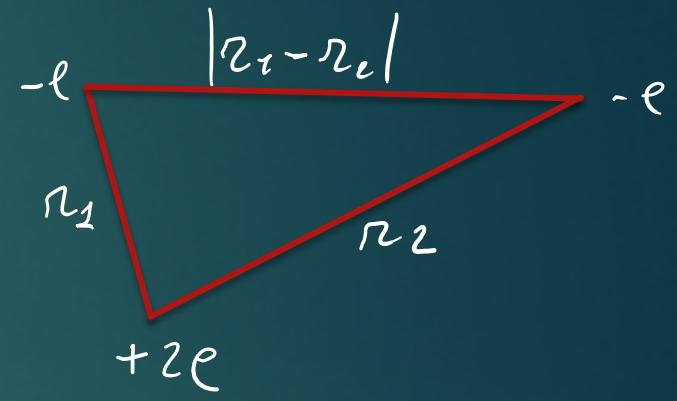


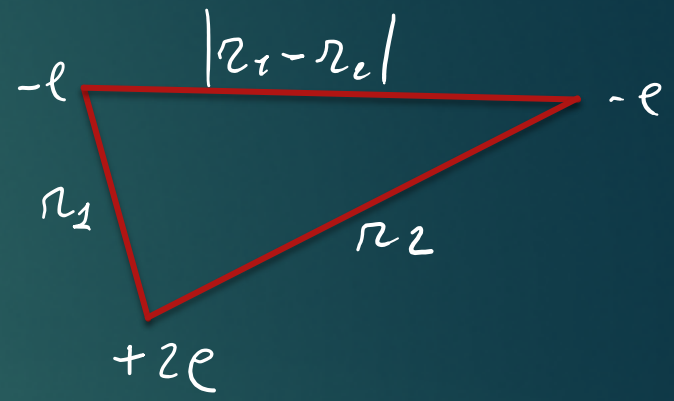

A significantly improved result can be obtained by keeping the same functional form, but replacing 2 by an adjustable parameter Z

$$\tilde{\psi}(r_1, r_2) \propto e^{-Z(r_1+r_2)}$$

# Helium atom

A significantly improved result can be obtained by keeping the same functional form, but replacing 2 by an adjustable parameter Z

$$\tilde{\Psi}(r_1, r_2) \propto e^{-Z(r_1+r_2)}$$




And by exploiting the variational principle:

$$\tilde{E} \geq \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle}$$

R for normalization

But, considering $\tilde{\Psi} = e^{-Z(r_1+r_2)}$ and

$$H = -\frac{\hbar^2}{2\,m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

# Helium atom

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no e-e interaction

correction

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2)\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

as before was $8E_1$

$\frac{1}{r}$ is calculated for an hydrogen atom with nuclear charge $+Ze$

Now

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \; ; \quad \langle V_{ee} \rangle = -\frac{5Z}{4} E_1 \; ;$$

# Helium atom

$$H = -\frac{\hbar^2}{2\,m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

no e-e interaction

correction

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} \quad ; \quad \langle V_{ee} \rangle = -\frac{5Z}{4} E_1 \quad ;$$

$$E_1 = \frac{-e^2}{8\pi\varepsilon_0 a}$$

$$\Rightarrow \langle H \rangle = 2Z^2 E_1 + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\frac{Z}{a} - \frac{5Z}{4} E_1 =$$

# Helium atom

$$H = -\frac{\hbar^2}{2\,m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

no e-e interaction

↓ correction

$$\langle H \rangle = \left(-2Z^2 + \frac{27}{4}Z\right) E_1$$

According to the variational principle I should minimize $\langle H \rangle$

$$\Rightarrow \frac{d\langle H \rangle}{dZ} = \left(-4Z + \frac{27}{4}\right) E_1 = 0 \Rightarrow 4Z = \frac{27}{4} \Rightarrow Z = \frac{27}{16}$$

# Helium atom

$$H = -\frac{\hbar^2}{2\,m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

no e-e interaction

correction

$$\langle H \rangle = \left(-2Z^2 + \frac{27}{4}Z\right)E_1$$

$$Z = \frac{27}{16} = 1{,}69$$

Physical interpretation: Z in the approximate wavefunction represents an *effective* nuclear charge. Each electron partially shields the other electron from the positively charged nucleus ...

Now the expected energy value is:

$$\langle H \rangle = \left(-2\,\frac{27^2}{16^2} + \frac{27^2}{4\cdot 16}\right)E_1 = 5{,}17\,E_1 = -74{,}5\,eV$$

2% discrepancy w.r.t. experiment