PX262 Quantum Mechanics

No.

Date

Formal postulates

① ∀ dynamical system ∃ a state function from which all possible predictions of the physical properties of the system can be obtained.

↳ State functions are often expressed as wavefunctions $\psi(r,t)$

↳ NOT experimentally accessible

↳ continuous, square-integrable, single-valued function

+ vectors in Hilbert space

+ normalized: $\int_\tau |\psi(r,t)|^2 d\tau = 1$

↳ Defn (inner product): $\langle \psi_1 | \psi_2 \rangle = \int_\tau \psi_1^* \psi_2 \, d\tau$

↳ Defn: ψ_m, ψ_n orthonormal if $\langle \psi_m | \psi_n \rangle = \delta_{mn}$.

↳ Superposition principle:

linear combination of (usually) eigenstates of chosen operator.

② Observables are dynamical variables of a quantum system accessible to measurement. Every observable is associated with an operator.

↳ In QM, operators associated with observables must be linear and Hermitian.

↳ Defn: Hermitian operator $\langle f | \hat{Q} g \rangle = \langle g^* | \hat{Q}^* f^* \rangle = \langle \hat{Q} f | g \rangle$

- Hermitian ⇒ real eigenvalues.

$$\hat{Q}\psi_n = q_n \psi_n \Rightarrow \begin{cases} \langle \psi_n | \hat{Q} \psi_n \rangle = q_n \langle \psi_n | \psi_n \rangle = q_n \\ \langle \psi_n^* | \hat{Q}^* \psi_n^* \rangle = q_n^* \langle \psi_n^* | \psi_n^* \rangle = q_n^* \langle \psi_n | \psi_n \rangle = q_n^* \end{cases}$$

$\hat{Q}$ Hermitian ⇒ $\langle \psi_n | \hat{Q} \psi_n \rangle = \langle \psi_n^* | \hat{Q}^* \psi_n^* \rangle \Rightarrow q_n = q_n^* \Rightarrow q_n \in \mathbb{R}$. □

- Hermitian operators have orthonormal eigenfunctions.

$\langle \psi_m | \hat{Q} \psi_n \rangle = \langle \psi_n^* | \hat{Q}^* \psi_m^* \rangle \Rightarrow q_n \langle \psi_m | \psi_n \rangle = q_m \langle \psi_m | \psi_n \rangle \Rightarrow \langle \psi_m | \psi_n \rangle = \delta_{mn}$. □

↳ Correspondence principle:

(i) QM predictions approach classical results at the classical limit.

(ii) We can construct operators based on relationships of corresponding classical dynamical variables (e.g. $E = T + V$, $T = p^2/2m$, $\hat{p} = -i\hbar\nabla \Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$)

↳ Defn: Commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

↳ $[\hat{A}, \hat{B}] = 0$ ⇒ operators commute ⇒ compatible ⇒ dynamical variables: ✗uncertainty.

- Compatible operators share a common set of eigenfunctions.

(⇒) measure both $\hat{A}, \hat{B}$ simultaneously to arbitrary precision ⇒ $\psi \searrow \psi_A$ eigenfunction of $\hat{B}$.

(⇐) $[\hat{A}, \hat{B}]\psi_n = \hat{A}\hat{B}\psi_n - \hat{B}\hat{A}\psi_n = b_n \hat{A}\psi_n - a_n \hat{B}\psi_n = b_n a_n \psi_n - a_n b_n \psi_n = 0$ □

No.

Date

(orbital)

↳ Angular momentum operators:

$$\begin{cases} \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \\ \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \end{cases} \Rightarrow [\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k \text{ , i.e. } \begin{cases} [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \\ [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \end{cases}$$

↳ $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ $\Rightarrow [\hat{L}_i, \hat{L}^2] = 0$ ↳ share a set of eigenfunctions $Y_{\ell m_\ell}(\theta, \phi)$

↳ (orbital angular momentum) ladder operators ($\hat{L}_z$):

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad , \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

$$\Rightarrow [\hat{L}^2, \hat{L}_\pm] = 0 \quad , \quad [\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm .$$

↳ $\hat{L}_\pm$ leaves L unchanged ($\hat{L}_\pm\hat{L}^2 Y_{\alpha\beta} = \alpha\hat{L}_\pm Y_{\alpha\beta} \Rightarrow \hat{L}^2(\hat{L}_\pm Y_{\alpha\beta}) = \alpha(\hat{L}_\pm Y_{\alpha\beta})$ $([\hat{L}^2, \hat{L}_\pm] = 0)$)

and changes L_z by $\pm\hbar$ ($\hat{L}_\pm\hat{L}_z Y_{\alpha\beta} = (\hat{L}_z\hat{L}_\pm \mp \hbar\hat{L}_\pm)Y_{\alpha\beta} = \beta\hat{L}_\pm Y_{\alpha\beta} \Rightarrow \hat{L}_z\hat{L}_\pm Y_{\alpha\beta} = (\beta\pm\hbar)\hat{L}_\pm Y_{\alpha\beta}$)

↳ eigenvalue spectrum found by solving $\hat{L}_-\hat{L}_+ Y_{\alpha\beta_{max}} = \hat{L}_+\hat{L}_- Y_{\alpha\beta_{min}} = 0$.

③ (4) The expectation value $\langle q\rangle$ of the observable represented by $\hat{Q}$ is

$$\langle q\rangle = \int_\tau \psi^*\hat{Q}\psi\, d\tau = \langle\psi|\hat{Q}\psi\rangle .$$

This is the mean value of an observable measured over many experiments, all starting with the same quantum state.

↳ uncertainty: standard deviation $\sigma_q = \sqrt{\langle q^2\rangle - \langle q\rangle^2}$

↳ generalized HUP:

(proof NE) $\sigma_q\sigma_r \geq \frac{1}{2}|\langle[\hat{Q},\hat{R}]\rangle| = \frac{1}{2i}\langle[\hat{Q},\hat{R}]\rangle$ e.g. $[\hat{x},\hat{p}_x] = i\hbar \Rightarrow \sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}$ (HUP)

↳ Ehrenfest theorem:

(proof NE) $$\frac{d\langle\hat{Q}\rangle}{dt} = \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle + \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle .$$

i.e. $\hat{Q}$ time-independent, compatible with $\hat{H}$ $\Rightarrow$ dynamical variable conserved.

④ (3) When a measurement is made of a dynamical variable, represented by $\hat{Q}$, the result must be one of the eigenvalues of $\hat{Q}$.

↳ The choice of eigenvalues obtained is probabilistic ($P(\psi\searrow\psi_n) \propto |c_n|^2$)

⑤ The time dependence of the wavefunction ψ is determined by the time-dependent Schrödingers equation $\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$ ($\hat{H}$ = Hamiltonian operator)

No.

Date

Density Functional Theory (DFT):

DFT reduces the complex many-electron problem of a material and the external influence from the static nuclei to a system of non-interacting electrons in effective fields.

Free electron model of a metal

Def: In a many-electron system, the energy of the highest occupied single particle state is the Fermi energy E_F, and its wavenumber is the Fermi wavenumber k_F. ← $\frac{\pi n_F}{L}$ $(N = 2n_F)$

↳ $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \Rightarrow N = \frac{2L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\sqrt{E_F} = \int_0^{E_F} n(E)\,dE$

⇒ Total energy:

$$E_{tot.} = \int_0^{E_F} E\,n(E)\,dE = \frac{2L}{3\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2} E_F^{3/2}$$

where $n(E)$ is the density of states

$$n(E) = \frac{dN}{dE} = \frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{\sqrt{E}} \quad (n(E) \propto 1/\sqrt{E})$$

⇒ Average energy per electron: $E_{tot}/N = E_F/3$

↳ 3D: Fermi surface is a sphere ⇒ $N = \frac{2 \times (\frac{4\pi}{3}k_F^3)}{(2\pi)^3/V} = \frac{Vk_F^3}{3\pi^2}$ (k_F = radius)

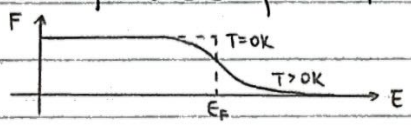
(spin; volume of sphere; volume per state)

⇒ $E_{avg.} = E_{tot}/N = \frac{3}{5}E_F$

where $k_F = (3\pi^2\rho)^{1/3}$ is the Fermi wavevector.

$$\Rightarrow n(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E} \quad (n(E) \propto \sqrt{E}).$$

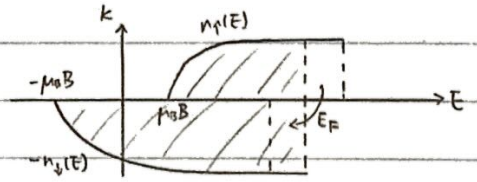
↳ Distribution of states of e^- (fermions): Fermi-Dirac distribution



$$F(E, \mu, T) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

Metal in a magnetic field

$$E_\uparrow = \frac{\hbar^2 k^2}{2m} + \mu_B B, \quad E_\downarrow = \frac{\hbar^2 k^2}{2m} - \mu_B B$$



NOTE: Fermi temperature: $T_F = E_F/k_B$ $(E_F = k_B T_F)$

Fermi velocity: $v_F = \hbar k_F/m$ $(p = mv_F = \hbar k_F)$

No.

Date

Electrons in crystalline structures

↳ A perfect crystal can be generated by decorating each point in a lattice with the same basis (atoms).

↳ In 3D: $\underline{R} = n_1\underline{a} + n_2\underline{b} + n_3\underline{c}$, $\underline{a}, \underline{b}, \underline{c}$ are primitive vectors.

↳ Volume of unit cell $= v_c = |\underline{a}\cdot(\underline{b}\times\underline{c})|$

- **Wigner - Seitz cells:**
  The cell constructed around a lattice point by planes that perpendicularly bisect the vectors connecting neighbouring points.

↳ **Reciprocal lattice:**

(FT) lattice with spacing $2\pi/a$. By periodicity, $e^{i\underline{G}_{h,k,l}\cdot\underline{R}_{n_1,n_2,n_3}} = 1$

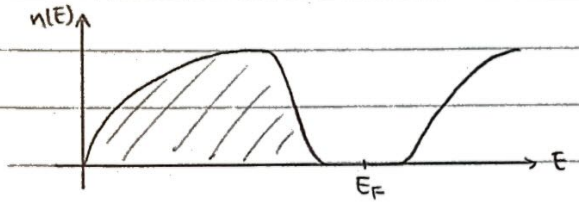
$\Rightarrow \underline{G}_{h,k,l} = h\underline{A} + k\underline{B} + l\underline{C}$.

$\underline{A} = \frac{2\pi(\underline{b}\times\underline{c})}{\underline{a}\cdot(\underline{b}\times\underline{c})}$, $\underline{B} = \frac{2\pi(\underline{c}\times\underline{a})}{\underline{a}\cdot(\underline{b}\times\underline{c})}$, $\underline{C} = \frac{2\pi(\underline{a}\times\underline{b})}{\underline{a}\cdot(\underline{b}\times\underline{c})}$ are the primitive vectors (in reciprocal space)

↳ The reciprocal lattice is measured directly via x-ray diffraction.

- **Brillouin zones:**
  Wigner - Seitz cells analogue in reciprocal space. (First Brillouin zone: $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$)

Metals, insulators and semiconductors

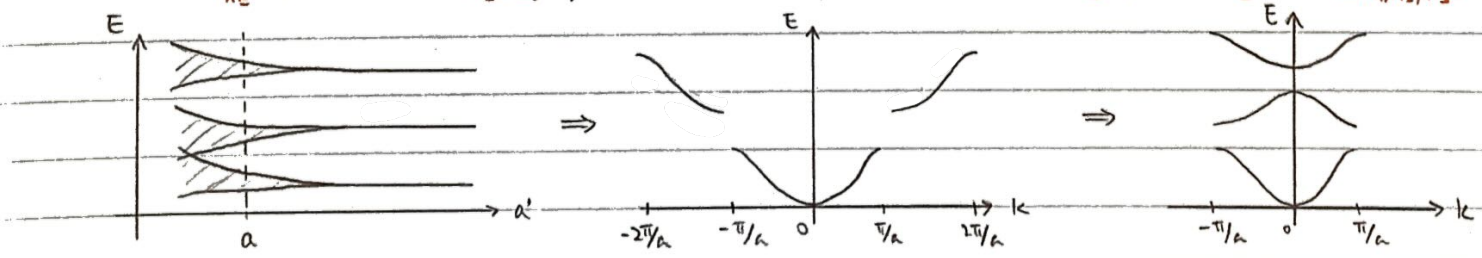


If the Fermi energy (E_F) lies in a gap (in the density of states), the material is an insulator.
(no states near $E_F \Rightarrow$ no conduction)

If the energy gap is of order $0 < \Delta \le 2eV$, the material is a semiconductor.

- **Bloch's theorem:**
  Solutions to the Schrödinger eqn in a periodic potential are of the form

$\psi_{n\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{n\underline{k}}(\underline{r})$, where u is periodic with $u_{n\underline{k}}(\underline{r}) = u_{n\underline{k}}(\underline{r} + \underline{R}_{n_1,n_2,n_3})$



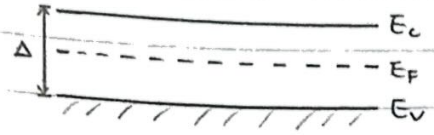
1st Brillouin zone

($\underline{k}' = \underline{k} - \underline{G}_{hkl}$)

No.

Date

Semiconductors



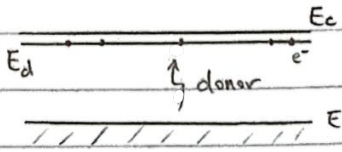
At finite T, a small proportion of the electrons will be thermally excited from the valence band to the conduction band, allowing the semiconductor to conduct.

↳ (group IV) $3s^2 3p^2$ $4s^2 4p^2$
Semiconductors (e.g. Si, Ge) are deliberately doped with a very low concentration of impurities (~ 1 in 10^5), which have either one more or one less valence electron per atom.

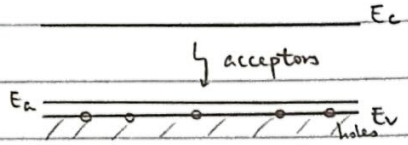
↳ donors: donate 1 electron, i.e. group V (e.g. P – $3s^2 3p^3$)

↳ acceptors: remove 1 electron, i.e. group III (e.g. Ga – $4s^2 4p^1$)

- (-ve) **n-type** semiconductors:
  The donor impurities introduces additional electronic states close to the bottom of the conduction band.
  ⇒ electrons are easily excited thermally into the conduction band from the new levels.

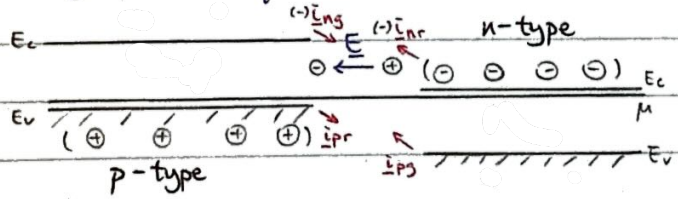


- (+ve) **p-type** semiconductors:
  The acceptors introduces 'holes' in the valence band, which are unfilled states just above the valence band.
  ⇒ electrons are easily excited thermally into these levels and leave behind holes, which are positively charged current carriers.



The p-n junction

Regions in equilibrium must have the same chemical potential μ. ($\mu \lesssim E_a$, $\mu \gtrsim E_d$)

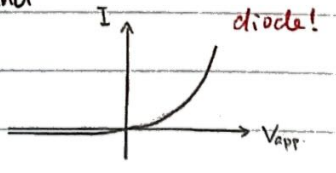


At equilibrium (zero bias),

$$\begin{cases} \underline{i}_{pr} + \underline{i}_{pg} = 0 \Rightarrow |\underline{i}_{pr}| = |\underline{i}_{pg}| \\ \underline{i}_{nr} + \underline{i}_{ng} = 0 \Rightarrow |\underline{i}_{nr}| = |\underline{i}_{ng}| \end{cases}$$

NOTE: $i_{ng} \propto e^{-\Delta/k_B T}$ ($\Delta/k_B T \gg 1$), i.e. $i_{ng} \propto$ probability of exciting a minority carrier, e^-, in the p-type region.
(similarly, $i_{pg} \propto e^{-\Delta/k_B T}$)

↳ Apply a forward bias ⇒ $\underline{E}\downarrow$: $\Delta E = -eV_{app}$.
⇒ i_{nr}, i_{pr} (recombination currents) increased by a factor of $e^{eV_{app}/k_B T}$ and i_{ng}, i_{pg} (generation currents) are left unchanged.
⇒ net hole current: $|\underline{i}_p| = |\underline{i}_{pr} + \underline{i}_{pg}| = |\underline{i}_{pg}|\,(\exp(eV_{app}/k_B T) - 1)$
net electron current: $|\underline{i}_n| = |\underline{i}_{nr} + \underline{i}_{ng}| = |\underline{i}_{ng}|\,(\exp(eV_{app}/k_B T) - 1)$
⇒ Total current: $I = i_p + i_n = i_s(\exp(eV_{app}/k_B T) - 1)$ ($i_s = |\underline{i}_{ng}| + |\underline{i}_{pg}|$)



No.

Date

Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

↳ Properties:

- $\sigma_i^2 = I$ $\quad (\hat{S}_i = \frac{\hbar}{2}\sigma_i \Rightarrow [\hat{S}_i, \hat{S}_j] = i\hbar\varepsilon_{ijk}\hat{S}_k)$
- $[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k \Rightarrow [\sigma_x, \sigma_y] = 2i\sigma_z, \; [\sigma_y, \sigma_z] = 2i\sigma_x, \; [\sigma_z, \sigma_x] = 2i\sigma_y.$
- anticommutativity: $\sigma_i\sigma_j + \sigma_j\sigma_i = 0 \quad (i \neq j) \;\sim\; \underline{\text{OR}} \;\; \{\sigma_i, \sigma_j\} = 2\delta_{ij} I$

Relativistic QM

↳ Relativity: $E^2 = p^2c^2 + m^2c^4$, correspondence principle: $E \mapsto i\hbar\frac{\partial}{\partial t}$, $\underline{p} \mapsto -i\hbar\underline{\nabla}$.

$$\Rightarrow \quad -\hbar^2\frac{\partial^2\psi}{\partial t^2} = -\hbar^2c^2\underline{\nabla}^2\psi + m^2c^4\psi \qquad \text{(Klein–Gordon equation)}$$

Problem: $E = \pm\sqrt{p^2c^2 + m^2c^4}$. In QM, we need all solns for a complete set of solns.

↳ Probability density $\rho = \psi^*\psi$ is proportional to $E \Rightarrow$ non-physical −ve probabilities.

↳ K-G eqn is second-order (∂_t^2), while TDSE is first order (∂_t)

$(i\hbar\gamma^\mu\partial_\mu\psi - mc\psi = (i\not{\partial} - m)\psi = 0)$

↳ Dirac equation: $\quad (c\underline{\alpha}\cdot\underline{p} + \beta mc^2)\psi(\underline{r}, t) = i\hbar\frac{\partial}{\partial t}\psi(\underline{r}, t)$

$\underline{\text{OR}} \quad (-i\hbar c\underline{\alpha}\cdot\underline{\nabla} + \beta mc^2)\psi(\underline{r}, t) = i\hbar\frac{\partial}{\partial t}\psi(\underline{r}, t)$

where $\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}, \; \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}, \; \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}, \; \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$

Successes:

- In the non-relativistic limit, the Dirac eqn reduces to the TDSE with particle spins $\Rightarrow$ spins (and SOC) explained!
- Its interpretation (Dirac Sea interpretation) of negative energy states led to predictions of anti-particles (e.g. positron). ~ later improved upon in QFT.

No.

Date

Nuclear matter

A nucleus can be modelled roughly as a sphere of radius

$$R = R_0 A^{1/3}$$

where $R_0 \approx 1.2 \times 10^{-15}$ m, A is the mass number $A = Z + N$ (Z: atomic no., N: no. of neutrons)

↳ NOTATION: ${}^{A}_{Z}X$

↳ NOTE: All atomic masses are less than the sum of their parts owing to the forces keeping the nucleons together, i.e. $Au < Zm_p + Zm_e + Nm_n$.

Defn: The binding energy of a nucleus is the minimum energy required to separate it into its protons and neutrons, and is given by

$$E_B = (Zm_p + Nm_n)c^2 - {}^{A}_{Z}Mc^2$$

- NOTE: neutrons and protons are also fermions (both with spin $\hbar/2$).

↳ Protons and neutrons are bound together in nuclei by the strong interaction (against electrostatic repulsion)

↳ Properties of the strong interaction:
- independent of electric charge
- short-ranged ($\sim 10^{-15}$ m)
- nuclear matter has near-constant density and near-constant binding energy per nucleon E_B/A.
  ↳ E_B/A = 7–9 MeV for stable nuclei

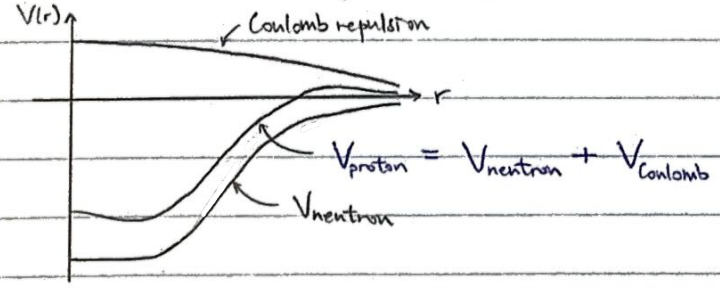
The liquid drop model

$$E_B = C_1 A - C_2 A^{2/3} - C_3 \frac{Z(Z-1)}{A^{1/3}} - C_4 \frac{(A-2Z)^2}{A} \pm C_5 A^{-4/3}$$

NOTE: $N = A - Z \neq A$!

$\pm$ ↳
- $+$ if $Z, N \in 2\mathbb{N}$
- $-$ if $Z, N \in 2\mathbb{N}+1$
- 0 otherwise.

The shell model (spherically symmetric)



Analogous to electrons: (noble gases)

$1s^2 \mid 2s^2 2p^6 \mid 3s^2 3p^6 \mid 4s^2 3d^{10} 4p^6 \mid 5s^2 4d^{10} 5p^6 4f^{14} \mid \dots$

2 (2) He; 8; 10 (10) Ne; 8; 18 (18) Ar; 18; 36 (36) Kr; 32; 54 (54) Xe

⇓

Nuclei with magic numbers of neutrons and protons are very stable.

↳ 2, 8, 20, 28, 50, 82, 126