Symmetries. Active $\hat{T}_S\psi(\mathbf{r},t)=\psi(S\mathbf{r},t)=\psi(\mathbf{r}',t)$. Passive $\hat{O}\to\hat{T}_S^\dagger\hat{O}\hat{T}_S$. The system is invariant under $\hat{T}_S$ if $\hat{O}=\hat{T}_S^\dagger\hat{O}\hat{T}_S$. Momentum generator $\psi(\mathbf{r})\to\psi(\mathbf{r}-\varepsilon)\approx\psi(\mathbf{r})-\varepsilon\cdot\nabla\psi(\mathbf{r})=\psi(\mathbf{r})-\frac{i}{\hbar}\varepsilon\cdot\hat{\mathbf{p}}\psi(\mathbf{r})\Rightarrow T_\varepsilon=\hat{I}-\frac{i}{\hbar}\cdot\hat{\mathbf{p}}$. Translational invariant $[\hat{p}_i,\hat{O}]=0$. Hamiltonian generator $\psi(\mathbf{r},t)\to\psi(\mathbf{r},t-\delta t)\approx\psi(\mathbf{r},t)+\delta t\frac{i}{\hbar}\hat{H}\psi(\mathbf{r},t)\Rightarrow\hat{T}_{\delta t}=\hat{I}+\frac{i}{\hbar}\delta t\hat{H}$. Time translation invariant $[\hat{H},\hat{O}]=0$. Angular momentum generator $\hat{R}_z(\delta\theta)\approx\left(\begin{smallmatrix}1&-\delta\theta&0\\\delta\theta&1&0\\0&0&1\end{smallmatrix}\right)=I-\delta\theta S_3$. $\hat{R}_z(\delta\theta)=\hat{I}+\frac{i}{\hbar}\delta\theta\hat{L}_z$. Rotational invariant $[\hat{\mathbf{L}},\hat{O}]=0$.

Unitary operators. Finite translation operators $\hat{U}_{\mathbf{a}}=e^{-i\mathbf{a}\cdot\hat{\mathbf{p}}/\hbar}$, $\hat{U}(t)=e^{-i\hat{H}t/\hbar}$, $\hat{U}_\theta=e^{i\boldsymbol{\theta}\cdot\hat{\mathbf{L}}/\hbar}$. Parity $\hat{P}=\psi(\mathbf{r},t)=\psi(-\mathbf{r},t)$. $\langle\phi|\hat{P}^\dagger\hat{\mathbf{r}}\hat{P}|\psi\rangle=-\langle\phi|\hat{\mathbf{r}}|\psi\rangle\Rightarrow\hat{P}^\dagger\hat{\mathbf{r}}\hat{P}=-\hat{\mathbf{r}}$, $\hat{P}^\dagger\hat{\mathbf{p}}\hat{P}=-\hat{\mathbf{p}}$. A system is invariant under spatial inversion if $[\hat{H},\hat{P}]=0$. Time reversal $\hat{T}\psi(\mathbf{r},t)=\psi^*(\mathbf{r},t)$. $\psi(\mathbf{r},t)=U(t)\psi(\mathbf{r},0)=e^{-i\hat{H}t/\hbar}\psi(\mathbf{r},0)\Rightarrow\psi^*(\mathbf{r},t)=e^{i\hat{H}t/\hbar}\psi^*(\mathbf{r},0)$. $\hat{T}[\hat{H},\hat{T}]=\hat{T}^\dagger\hat{H}\hat{T}-\hat{T}^\dagger\hat{T}\hat{H}=\hat{H}^*-\hat{H}$. System has time reversal symmetry if $\hat{H}$ is real. $\hat{T}^\dagger\hat{\mathbf{r}}\hat{T}=\hat{\mathbf{r}}$, $\hat{T}^\dagger\hat{\mathbf{p}}\hat{T}=-\hat{\mathbf{p}}$. Antiunitary operators $\hat{O}^\dagger\hat{O}=\hat{I}$ but $\hat{O}\lambda=\lambda^*\hat{O}$. $\hat{P}^\dagger i\hbar\delta_{ij}\hat{P}=\hat{P}^\dagger\left[\hat{r}_i,\hat{p}_j\right]\hat{P}=\left[\hat{P}^+\hat{r}_i\hat{P},\hat{P}^\dagger\hat{p}_j\hat{P}\right]=\left[-\hat{r}_i,-\hat{p}_j\right]=i\hbar\delta_{ij}$, $\hat{T}^+i\hbar\delta_{ij}\hat{T}=\hat{T}^\dagger\left[\hat{r}_i,\hat{p}_j\right]\hat{T}=\left[\hat{T}^\dagger\hat{r}_i\hat{T},\hat{T}^\dagger\hat{p}_j\hat{T}\right]=\left[\hat{r}_i,-\hat{p}_j\right]=-i\hbar\delta_{ij}$. $\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi|\hat{O}|\psi\rangle=\frac{i}{\hbar}\langle\psi|[\hat{H},\hat{O}]|\psi\rangle+\langle\psi|\frac{\partial\hat{O}}{\partial t}|\psi\rangle$. If $\hat{O}$ has no explicit time dependence, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi|\hat{O}|\psi\rangle=\frac{i}{\hbar}\langle\psi|[\hat{H},\hat{O}]|\psi\rangle$. If the observable commutes with $\hat{H}$, its expectation value is conserved for any $|\psi\rangle$. For time independent Hamiltonians, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi|\hat{H}|\psi\rangle=0\Rightarrow$ conservation of energy. For translationally-invariant Hamiltonians $[\hat{H},\hat{\mathbf{p}}]=0\Rightarrow$ conservation of momentum.

Euler angles. If $[\hat{A},\hat{B}]\neq0$, $e^{\hat{A}+\hat{B}}\neq e^{\hat{A}}e^{\hat{B}}$. (i) Rotate the system about z by $\gamma\in[0,2\pi]$. (ii) Rotate about x by $\beta\in[0,\pi]$. (iii) Rotate about z by $\alpha\in[0,2\pi]\Rightarrow$ Unitary operator $\hat{U}_{\alpha,\beta,\gamma}\psi(\mathbf{r})=\psi\left(R_z(\alpha)R_x(\beta)R_z(\gamma)\mathbf{r}\right)=e^{i\alpha\hat{L}_z/\hbar}e^{i\beta\hat{L}_x/\hbar}e^{i\gamma\hat{L}_z/\hbar}\psi(\mathbf{r})$ (consecutive rotations). In the $|l,m\rangle$ basis, $\hat{U}_{\alpha,\beta,\gamma}=\sum_{m=-l}^{l}\sum_{m'=-l}^{l}|l,m\rangle\langle l,m|\hat{U}_{\alpha,\beta,\gamma}|l,m'\rangle\langle l,m'|$. $D^l_{m,m'}(\alpha,\beta,\gamma)=\langle l,m|\hat{U}_{\alpha,\beta,\gamma}|l,m\rangle=\langle l,m|e^{i\alpha\hat{L}_z/\hbar}e^{i\beta\hat{L}_x/\hbar}e^{i\gamma\hat{L}_z/\hbar}|l,m'\rangle$. $e^{i\gamma\hat{L}_z/\hbar}|l,m'\rangle=e^{i\gamma m'}|l,m'\rangle$, $\langle l,m|e^{i\alpha\hat{L}_z/\hbar}=e^{i\alpha m}\langle l,m|$. $D^l_{m,m'}(\alpha,\beta,\gamma)=e^{i(\alpha m+\gamma m')}\langle l,m|e^{i\beta\hat{L}_x/\hbar}|l,m'\rangle=e^{i(\alpha m+\gamma m')}d^l_{m,m'}(\beta)$.

Time-dependent perturbation theory. $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle=\hat{H}|\psi(t)\rangle=\left(\hat{H}_0+\lambda\hat{V}(t)\right)|\psi(t)\rangle$. Expand $|\psi(t)\rangle=\sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle$. $\Rightarrow\sum_n i\hbar\frac{\mathrm{d}c_n(t)}{\mathrm{d}t}e^{-iE_nt/\hbar}=\lambda\sum_n\hat{V}(t)c_n(t)e^{-iE_nt/\hbar}\Rightarrow i\hbar\frac{\mathrm{d}c_m(t)}{\mathrm{d}t}=\lambda\sum_n c_n(t)e^{i\omega_{mn}t}\langle m|\hat{V}(t)|n\rangle$, where $\omega_{mn}=\frac{E_m-E_n}{\hbar}$. Perturbative expansion. Assume $|\psi(t_0)\rangle=|i\rangle$, $c_n(t_0)=\delta_{ni}$, $c_n(t)=c_n^{(0)}(t)+\lambda c_n^{(1)}(t)+\lambda^2c_n^{(2)}(t)+\cdots\Rightarrow i\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_m^{(0)}(t)=0\Rightarrow c_m^{(0)}(t)=c_m^{(0)}(t_0)$. At first order, $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_m^{(1)}(t)=e^{i\omega_{mi}t}\langle m|\hat{V}(t)|i\rangle$ with solution $c_m^{(1)}(t)=-\frac{i}{\hbar}\int_{t_0}^t\mathrm{d}t'e^{i\omega_{mi}t'}\langle m|\hat{V}(t')|i\rangle$. $|\psi(t)\rangle\approx\sum_n\left[\delta_{ni}+c_n^{(1)}(t)\right]e^{-iE_nt/\hbar}|n\rangle$. The probability that at $t>t_0$, a measurement of the state $|\psi(t)\rangle$ yields $|f\rangle$ is $P_f(t)=\left|\langle f|\psi(t)\rangle\right|^2=\left|c_f^{(1)}(t)\right|^2$.

Example. Adiabatic perturbation. $\hat{H}=\hat{H}_0+\hat{V}e^{t/\tau}$, where $\hat{V}$ switches on continuously from $\hat{H}=\hat{H}_0$ at $t=-\infty$ to $\hat{H}=\hat{H}+\hat{V}$ at $t=0$. $c_n^{(1)}(0)=-\frac{i}{\hbar}\langle n|\hat{V}|i\rangle\int_{-\infty}^0\mathrm{d}te^{t/\tau}e^{i\omega_{ni}t}=-\frac{i}{\hbar}\frac{\langle n|\hat{V}|i\rangle}{1/\tau+i\omega_{ni}}$. In the limit $\tau\to\infty$, $c_n^{(1)}(0)=\frac{\langle n|\hat{V}|i\rangle}{E_i-E_n}$.

Example. $\hat{H}=\hat{H}_0+\hat{V}e^{-t^2/\tau^2}$ which switches continuously from $\hat{H}_0$ at $t=-\infty$ to $\hat{H}=\hat{H}_0+\hat{V}$ at $t=0$, and back to $\hat{H}_0$ at $t=\infty$. $c_n^{(1)}(\infty)=-\frac{i}{\hbar}\langle n|\hat{V}|i\rangle\int_{-\infty}^{\infty}\mathrm{d}te^{-t^2/\tau^2}e^{i\omega_{ni}t}=-\frac{i}{\hbar}\langle n|\hat{V}|i\rangle e^{-\omega_{ni}^2\tau^2/4}\sqrt{\pi}\tau$. $P_f(\infty)=\frac{\pi\tau^2}{\hbar^2}\left|\langle f|\hat{V}|i\rangle\right|^2e^{-\omega_{fi}^2\tau^2/2}$.

Example. Hydrogen atom in ground state. $\psi_{100}(r)=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$ and final state $\psi_{210}=\frac{r}{\sqrt{32\pi a_0^5}}e^{-r/2a_0}\cos\theta$. At $t=0$, turn on an electric field in the $z-$direction which decays over time $E(t)=E_0e^{-t/\tau}$. In the electric dipole approximation $\hat{V}(t)=-\mathbf{d}\cdot\mathbf{E}(t)=er\cos\theta E_0e^{-t/\tau}$. $c^{(1)}=-\frac{i}{\hbar}\int_0^t\mathrm{d}t'\langle\psi_{210}|\hat{V}(t)|\psi_{100}\rangle e^{i\omega t'}=-\frac{ieE_0A}{\hbar}\frac{e^{(i\omega-1/\tau)t}-1}{i\omega-1/\tau}$, where $\omega=\frac{E_2-E_1}{\hbar}$. In the long time limit, $P(\infty)=\frac{e^2E_0^2A^2}{\hbar^2\omega^2+\hbar^2/\tau^2}$. For $\tau\to0$, $P(\infty)\to0$. For $\tau\to\infty$, $P(\infty)\to\frac{e^2E_0^2A^2}{\hbar^2\omega^2}$.

Fermi's golden rule. Oscillatory perturbation $\hat{V}(t)=\begin{cases}0 & t\le0\\ \hat{V}_0e^{-i\omega t}, & t>0\end{cases}$. $c_f^{(1)}(t)=-\frac{i}{\hbar}\int_0^t\mathrm{d}t'e^{i\omega_{fi}t'}\langle f|\hat{V}(t')|i\rangle=\frac{\langle f|\hat{V}_0|i\rangle}{\hbar}\frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}$. $P_{i\to f}(t)=\frac{t^2}{\hbar^2}\left|\langle f|\hat{V}_0|i\rangle\right|^2\mathrm{sinc}^2\left[\frac{(\omega_{fi}-\omega)t}{2}\right]$. In the long-time limit, $\lim_{t\to\infty}t\,\mathrm{sinc}^2\frac{xt}{2}=2\pi\delta(x)$. $P=\frac{2\pi t}{\hbar^2}\left|\langle f|\hat{V}_0|i\rangle\right|^2\delta(\omega_{fi}-\omega)$. The probability grows linearly with t. The transition rate $R_{i\to f}(t)=\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{2\pi}{\hbar}\left|\langle f|\hat{V}_0|i\rangle\right|^2\delta(E_{fi}-\hbar\omega)$. In the long-time limit, only a perturbation with frequency that matches ω_{fi} can induce transition from $|i\rangle$ to $|f\rangle$. Energy is absorbed from the perturbing field. If $\hat{V}(t)=\hat{V}_0e^{i\omega t}$ then energy is given up to the field (stimulated emission). If $\hat{V}(t)=\Theta(t)eE_0(\omega)\cos(\omega t)\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}=\frac{eE_0(\omega)}{2}\left(e^{i\omega t}+e^{-i\omega t}\right)\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}$ Then $R_{i\to f}=\frac{\pi e^2}{2\hbar^2}\int_0^\infty\mathrm{d}\omega E_0^2(\omega)\left|\langle f|\varepsilon\cdot\hat{\mathbf{r}}|i\rangle\right|^2\left[\delta(\omega_{fi}-\omega)+\delta(\omega_{fi}+\omega)\right]=\frac{\pi e^2}{2\hbar^2}E_0^2(|\omega_{fi}|)\left|\langle f|\varepsilon\cdot\hat{\mathbf{r}}|i\rangle\right|^2$.

Selection rules. For electric dipole transitions to be allowed, $\langle f|\epsilon\cdot\hat{\mathbf{r}}|i\rangle\neq0$. For Hydrogen-like states, consider $\left\langle n',l',s',j',m_j'|\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}|n,l,s,j,m_j\right\rangle$. $s=s'=\frac{1}{2}$, $j=l\pm\frac{1}{2}$. In the spherical basis, $\hat{\mathbf{r}}=\sqrt{4\pi}r\left(Y_1^1\mathbf{e}_-+Y_1^0\mathbf{e}_0+Y_1^{-1}\mathbf{e}_+\right)\Rightarrow\Delta j=0,\pm1$. $\Delta m_j=0,\pm1$. Parity $\Rightarrow\Delta l=\pm1$.

For multi-electron atoms. $\Delta J = 0, \pm 1$, $\Delta M_J = 0, \pm 1$, $\Delta L = 0, \pm 1$, $\Delta S = 0$.

Charged particle in EM fields. $\mathbf{E} = -\nabla\Phi(\mathbf{r},t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t)$. $\mathbf{B}(\mathbf{r},t) = \nabla\times\mathbf{A}(\mathbf{r},t)$. Lagrangian $\mathscr{L} = \frac{1}{2}m\dot{\mathbf{r}}^2 - q\Phi(\mathbf{r},t) + q\mathbf{A}(\mathbf{r},t)\cdot\dot{\mathbf{r}}$. Canonical momentum $\mathbf{p} = m\dot{\mathbf{r}} + q\mathbf{A}(\mathbf{r},t)$. Classical Hamiltonian $\mathscr{H} = \mathbf{p}\cdot\dot{\mathbf{r}} - \mathscr{L}$. Quantum Hamiltonian $\hat{H} = \left(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}},t)\right)^2 + q\Phi(\hat{\mathbf{r}},t)$. Conservation of momentum for $\Phi(\hat{\mathbf{r}},t) = 0$. The canonical momentum $[\hat{H},\hat{p}_i] \neq 0$. The kinetic momentum $[\hat{H}, \mathbf{p} - q\mathbf{A}(\hat{\mathbf{r}},t)] = 0$.

Gauge transformations. $\Phi(\hat{\mathbf{r}},t) \to \Phi(\hat{\mathbf{r}},t) - \frac{\partial\lambda(\hat{\mathbf{r}},t)}{\partial t}$, $\mathbf{A}(\hat{\mathbf{r}},t) \to \mathbf{A}(\hat{\mathbf{r}},t) + \nabla\lambda(\hat{\mathbf{r}},t)$. $\hat{H} \to \hat{H}_\lambda = \frac{1}{2m}\left[\hat{\mathbf{p}} - q(\mathbf{A}(\hat{\mathbf{r}},t) + \nabla\lambda(\hat{\mathbf{r}},t))\right]^2 + q\left(\Phi(\hat{\mathbf{r}},t) - \frac{\partial\lambda(\hat{\mathbf{r}},t)}{\partial t}\right)$. $\hat{G}_\lambda \equiv \exp\left(\frac{iq}{\hbar}\lambda(\hat{\mathbf{r}},t)\right)$. $\hat{G}_\lambda\hat{\mathbf{r}}\hat{G}_\lambda^\dagger = \hat{\mathbf{r}}$, $\hat{G}_\lambda\hat{\mathbf{p}}\hat{G}_\lambda^\dagger = \hat{\mathbf{p}} - q\nabla\lambda(\hat{\mathbf{r}},t)$. Applying on TDSE, $\hat{G}_\lambda i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{G}_\lambda\hat{H}\hat{G}_\lambda^\dagger\hat{G}_\lambda|\psi\rangle$. Using $\frac{\partial}{\partial t}\hat{G}_\lambda|\psi\rangle$ and $\hat{G}_\lambda\hat{\mathbf{p}}\hat{G}_\lambda^\dagger$ $\Rightarrow i\hbar\frac{\partial}{\partial t}|\psi_\lambda\rangle = \hat{H}_\lambda|\psi_\lambda\rangle$, $|\psi_\lambda\rangle = \hat{G}_\lambda|\psi\rangle$. $\hat{H}_\lambda = \hat{G}_\lambda\hat{H}\hat{G}_\lambda^\dagger + i\hbar\frac{\partial\hat{G}_\lambda}{\partial t}\hat{G}_\lambda^\dagger = \frac{1}{2m}\left[\hat{\mathbf{p}} - q\mathbf{A}_\lambda(\hat{\mathbf{r}},t)\right]^2 + q\Phi_\lambda(\hat{\mathbf{r}},t)$. For any observable $\hat{O}$, $\langle\psi|\hat{O}|\psi\rangle = \langle\psi|\hat{G}_\lambda^\dagger\hat{G}_\lambda\hat{O}\hat{G}_\lambda^\dagger\hat{G}_\lambda|\psi\rangle = \langle\psi_\lambda|\hat{O}'|\psi_\lambda\rangle$. An operator with $\hat{O} = \hat{O}' = \hat{G}_\lambda\hat{O}\hat{G}_\lambda^\dagger$ is a gauge invariant, e.g. $\mathbf{E}(\mathbf{r},t), \mathbf{B}(\mathbf{r},t)$. $\hat{O} \xrightarrow{\text{Direct gauge trans.}} \hat{O}_\lambda$. $\hat{O} \xrightarrow{\text{unitary operation}} \hat{O}'$. If $\hat{O}' = \hat{O}_\lambda$, $\langle\phi|\hat{O}|\psi\rangle \to \langle\phi_\lambda|\hat{O}_\lambda|\psi_\lambda\rangle = \langle\phi_\lambda|\hat{O}'|\psi_\lambda\rangle = \langle\phi|\hat{G}_\lambda^\dagger\hat{O}'\hat{G}_\lambda|\psi\rangle = \langle\phi|\hat{O}|\psi\rangle$. Such observables are true physical quantities. $G_\lambda m\dot{\mathbf{r}}G_\lambda^\dagger = \hat{G}_\lambda(\mathbf{p} - q\mathbf{A}(\hat{\mathbf{r}},t))\hat{G}_\lambda^\dagger = \hat{\mathbf{p}} - q\nabla\lambda(\hat{\mathbf{r}},t) - q\mathbf{A}(\hat{\mathbf{r}},t) = \mathbf{p} - q\mathbf{A}_\lambda(\hat{\mathbf{r}},t)$. Position and mechanical momentum are the same in all gauges. $\hat{H}_\lambda = \hat{G}_\lambda\hat{H}\hat{G}_\lambda^\dagger + i\hbar\frac{\partial\hat{G}_\lambda}{\partial t}\hat{G}_\lambda^\dagger \neq \hat{G}_\lambda\hat{H}\hat{G}_\lambda^\dagger$. By including dynamical variables of the field, the Hamiltonian would be time independent $\Rightarrow \hat{H}_\lambda = \hat{G}_\lambda\hat{H}\hat{G}_\lambda^\dagger$. TISE $\hat{H}|\psi\rangle = E|\psi\rangle \Rightarrow \hat{G}_\lambda\hat{H}|\psi\rangle = E\hat{G}_\lambda|\psi\rangle \Rightarrow \hat{H}_\lambda|\psi_\lambda\rangle = E|\psi_\lambda\rangle$.

Goppert-Mayer transformation. $\mathbf{E}(\mathbf{r},t) = -\frac{\partial\mathbf{A}(\mathbf{r},t)}{\partial t}$. In the long wavelength limit, $\mathbf{E}(\mathbf{0},t) = -\frac{\mathrm{d}\mathbf{A}(\mathbf{0},t)}{\mathrm{d}t}$, $\mathbf{B}(\mathbf{r},t) = \nabla\times\mathbf{A}(\mathbf{0},t) = 0$. $\hat{H} = \frac{1}{2m}\left[\hat{\mathbf{p}} - q\mathbf{A}(\mathbf{0},t)\right]^2 + V(\hat{\mathbf{r}})$. Let $\lambda(\hat{\mathbf{r}},t) = -\hat{\mathbf{r}}\cdot\mathbf{A}(\mathbf{0},t)$, $\hat{G}_\lambda\hat{\mathbf{p}}\hat{G}_\lambda^\dagger = \hat{\mathbf{p}} + q\mathbf{A}(\mathbf{0},t)$. $\hat{H}_\lambda = \frac{1}{2m}\hat{\mathbf{p}}^2 + V(\hat{\mathbf{r}}) + q\hat{\mathbf{r}}\cdot\frac{\mathrm{d}\mathbf{A}(\mathbf{0},t)}{\mathrm{d}t}$. Define $\hat{\mathbf{d}} = q\hat{\mathbf{r}} \Rightarrow$ $\hat{H}_\lambda = \frac{1}{2m}\hat{\mathbf{p}}^2 + V(\hat{\mathbf{r}}) - \hat{\mathbf{d}}\cdot\mathbf{E}(\mathbf{0},t)$ (electric dipole approximation).

Landau levels. $\mathbf{B} = (0,0,B)$, choose $\mathbf{A} = (0,Bx,0)$, $\Phi = 0$. Then $\hat{H} = \frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A})^2 = \frac{1}{2m}\left[\hat{p}_x^2 + (\hat{p}_y - qBx)^2 + \hat{p}_z^2\right]$. $[\hat{p}_z,\hat{H}] = 0 \Rightarrow$ $\psi(x,y,z) = \psi(x,y)e^{ik_z z}$. In $x-y$ plane, $\hat{H} = \frac{1}{2m}\left[\hat{p}_x^2 + \hat{p}_y^2 + q^2B^2x^2 - 2qBx\hat{p}_y\right]$. $[\hat{p}_y,\hat{H}] = 0 \Rightarrow \psi(x,y) = \psi_{k_y}e^{ik_y y}$, $k_y = \frac{p_y}{\hbar}$. $\Rightarrow \left[\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2(x-x_0)^2\right]\psi_{k_y}(x) = E\psi_{k_y}(x)$, where $\omega_c = \frac{qB}{m}$, $x_0 = \frac{\hbar k_y}{qB} \Rightarrow \psi_{k_y}(x) = \Phi_n(x-x_0)$, $\psi(x,y) = \Phi_n(x-x_0)e^{ik_y y}$, $E_{n,k_y} = \hbar\omega_c\left(n + \frac{1}{2}\right)$. The set of degenerate states for a fixed n is called a Landau level. $\psi(x,y,z) = \Phi_n(x-x_0)e^{ik_y y}e^{ik_z z}$. The TDSE in the full dimension: $\frac{1}{2m}\left[\hat{p}_x^2 + q^2B^2\left(x - \frac{\hbar k_y}{qB}\right)^2 + \hbar^2k_z^2\right]\psi_{k_y}(x) = E\psi_{k_y}(x)$ with $E_{n,k_y} = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2k_z^2}{2m}$. In a L_xL_y finite region, $\psi(x,y,z) = \psi(x,y+L_y,z) \Rightarrow k_y = \frac{2\pi n_y}{L_y}$. $k_y = \frac{qBx_0}{\hbar} \Rightarrow k_y \in \left[0, \frac{qBL_x}{\hbar}\right] \Rightarrow$ Available states $N = \frac{L_y}{2\pi}\int_0^{qBL_x/\hbar}\mathrm{d}k = \frac{qBA}{2\pi\hbar} \sim 10^{10}$. Choose $\mathbf{A} = (-yB,0,0)$. Two potentials differ by $\nabla\lambda = -(yB,Bx,0) \Rightarrow \lambda = -Bxy$, $\hat{G}_\lambda = e^{-iqBxy/\hbar}$. The TDSE in the new gauge: $\left[\frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega_c^2(y+y_0)^2\right]\psi_{k_x}(y) = E\psi_{k_x}(y)$, $y_0 = \frac{\hbar k_x}{qB}$. The eigenstates $\psi'(x,y) = e^{ik_x x}\Phi_n(y+y_0)$ with $E_{n,k_x} = \hbar\omega_c\left(n + \frac{1}{2}\right)$.

Spin. $\hat{\boldsymbol{\mu}} = -g_e\frac{e}{2m}\hat{\mathbf{S}} = -\frac{e}{m}\hat{\mathbf{S}}$. $\hat{H}_{\text{mag}} = -\hat{\boldsymbol{\mu}}\cdot\mathbf{B} = \frac{e}{m}\mathbf{B}\cdot\hat{\mathbf{S}} = \mu_B\mathbf{B}\cdot\boldsymbol{\sigma}$. For $\mathbf{B} = B\hat{\mathbf{z}}$, $\hat{H}_{\text{mag}} = \mu_B B\sigma_z = \begin{pmatrix}\mu_B B & 0\\ 0 & -\mu_B B\end{pmatrix}$. For the gauge choice $\mathbf{A} = (0,Bx,0)$, $\hat{H} = \frac{1}{2m}\left[\hat{p}_x^2 + q^2B^2\left(x - \frac{\hbar k_y}{qB}\right)^2 + \hbar^2k_z^2\right] + \frac{2}{\hbar}\mu_B B\hat{S}_z$. $[\hat{S}_z,\hat{H}] = 0$. Define $\hat{S}_z\chi = \pm\frac{\hbar}{2}\chi$. $E_{n,k_y} = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2k_z^2}{2m} \pm \mu_B B$.

Pauli equation. $\hat{S}_z\chi = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\chi = \varepsilon\chi$ has eigenstates $\frac{\hbar}{2}$ for $\chi_z^+ = \begin{pmatrix}1\\0\end{pmatrix}$ and $-\frac{\hbar}{2}$ for $\chi_z^- = \begin{pmatrix}0\\1\end{pmatrix}$. In this basis, $\chi_x^+ = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$, $\chi_x^- = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$, $\chi_y^+ = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}$, $\chi_y^- = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}$. The state space that describes both the spatial and spin: $|\psi\rangle = |\psi_1\rangle|\chi_z^+\rangle + |\psi_2\rangle|\chi_z^-\rangle$ such that $\langle\mathbf{r}|\psi\rangle = \psi_1(\mathbf{r},t)|\chi_z^+\rangle + \psi(\mathbf{r},t)|\chi_z^-\rangle$. In the spinor form, $\psi(\mathbf{r},t) = \begin{pmatrix}\psi_1(\mathbf{r},t)\\ \psi_2(\mathbf{r},t)\end{pmatrix}$. Hamiltonian in the enlarged space $\hat{H} = \begin{pmatrix}\hat{\mathbf{p}}^2/2m & 0\\ 0 & \hat{\mathbf{p}}^2/2m\end{pmatrix} = \frac{\hat{\mathbf{p}}^2}{2m}I_2$.

Pauli vector identity. $(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b}) = (\mathbf{a}\cdot\mathbf{b})I_2 + i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})$. $(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2 = \hat{\mathbf{p}}^2I_2 + i\boldsymbol{\sigma}\cdot(\hat{\mathbf{p}}\times\hat{\mathbf{p}}) = \hat{\mathbf{p}}^2I_2$. $\hat{H} = \frac{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2}{2m}$. Minimal-coupling substitution: $\hat{H} = \frac{\left(\boldsymbol{\sigma}\cdot(\hat{\mathbf{p}} - q\mathbf{A})\right)^2}{2m} = \frac{(\hat{\mathbf{p}} - q\mathbf{A})^2}{2m}I_2 + \frac{i}{2m}\boldsymbol{\sigma}\cdot\left[(\hat{\mathbf{p}} - q\mathbf{A})\times(\hat{\mathbf{p}} - q\mathbf{A})\right] = \frac{(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}},t))^2}{2m}I_2 - \frac{\hbar q}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}(\hat{\mathbf{r}},t) \Rightarrow \hat{H} = \frac{(\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}},t))^2}{2m}I_2 + \mu_B\boldsymbol{\sigma}\cdot\mathbf{B}(\hat{\mathbf{r}},t)$.

Pauli eq. for a spin-$\frac{1}{2}$ particle: $\left[\frac{(\boldsymbol{\sigma}\cdot(\hat{\mathbf{p}} - q\mathbf{A}))^2}{2m} + q\Phi I_2\right]\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$, or $\left[\frac{(\hat{\mathbf{p}} - q\mathbf{A})^2}{2m}I_2 - \frac{\hbar q}{2m}\boldsymbol{\sigma}\cdot\mathbf{B} + q\Phi I_2\right]\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$. For $\mathbf{B} = B\hat{\mathbf{z}}$, $\frac{1}{2m}\left[(\hat{\mathbf{p}} - q\mathbf{A})^2 - \hbar qB\right]\psi_1(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi_1(\mathbf{r},t)$, $\frac{1}{2m}\left[(\hat{\mathbf{p}} - q\mathbf{A})^2 + \hbar qB\right]\psi_2(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi_2(\mathbf{r},t)$.

The Klein-Gordon equation. $H^2 = c^2\mathbf{p}^2 + m^2c^4 \Rightarrow$ Free particle K-G equation $-\hbar^2\frac{\partial^2}{\partial t^2}\psi(\mathbf{r},t) = \left(-c^2\hbar^2\nabla^2 + m^2c^4\right)\psi(\mathbf{r},t)$. Different form: $\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \frac{m^2c^2}{\hbar^2}\right)\psi(\mathbf{r},t) = 0$ or $\left(\Box + \mu^2\right)\psi(\mathbf{r},t) = 0$. Free particle solutions $\psi(\mathbf{r},t) = Ne^{i(\mathbf{p}\cdot\mathbf{r} - E_p t)/\hbar} \Rightarrow E_{\mathbf{p}} = \pm\sqrt{c^2\mathbf{p}^2 + m^2c^4}$.

Non-relativistic limit. Write $\psi(\mathbf{r},t)=\phi(\mathbf{r},t)e^{-imc^2t/\hbar}\xrightarrow{\text{K-G}}\frac{1}{c^2}\frac{\partial^2\phi}{\partial t^2}-2i\frac{m}{\hbar}\frac{\partial\phi}{\partial t}-\nabla^2\phi=0\xrightarrow{c\to\infty} i\hbar\frac{\partial\phi}{\partial t}=-\frac{\hbar^2\nabla^2}{2m}\phi$.

Lorentz invariance. $\partial_\mu\partial^\mu=\partial^\mu\partial_\mu=\Box$ is a Lorentz invariant $\Rightarrow$ $\left[\partial_\mu\partial^\mu+\left(\frac{mc}{\hbar}\right)^2\right]\psi(\mathbf{r},t)=0$ is Lorentz invariant.

Probability currents. In non-relativistic QM, $\frac{\partial\rho(\mathbf{r},t)}{\partial t}+\nabla\cdot\mathbf{j}(\mathbf{r},t)=0$, where $\rho=\psi^*\psi$, $\mathbf{j}=-\frac{i\hbar}{2m}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right)$. The four-current $j^\mu=(c\rho,\mathbf{j})\Rightarrow\partial_\mu j^\mu=0$. In relativistic QM, K-G eq. $\Rightarrow$ $\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi=\nabla^2\psi-\left(\frac{mc}{\hbar}\right)^2\psi\Rightarrow\rho=\frac{i\hbar}{c}\left(\psi^*\frac{\partial}{\partial t}\psi-\psi\frac{\partial}{\partial t}\psi^*\right)$, $\mathbf{j}=-i\hbar c\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right)$. The four-current $j^\mu=i\hbar c\left(\psi^*\partial^\mu\psi-\psi\partial^\mu\psi^*\right)$. For $\psi=Ne^{i(\mathbf{p}\cdot\mathbf{r}-E_\mathbf{p}t)/\hbar}$, $j^\mu=2|N|^2(E_\mathbf{p},\mathbf{p})$.

K-G with external potential. $A^\mu=\left(\frac{\Phi}{c},\mathbf{A}\right)$, $A_\mu=\left(\frac{\Phi}{c},-\mathbf{A}\right)$. Minimal coupling substitution $\hat{\mathbf{p}}=-i\hbar\nabla\to-i\hbar\nabla-q\mathbf{A}$, $i\hbar\frac{\partial}{\partial t}\to i\hbar\frac{\partial}{\partial t}-q\Phi$. $\partial_\mu\to\partial_\mu+\frac{iq}{\hbar}A_\mu$, $\partial^\mu\to\partial^\mu+\frac{iq}{\hbar}A^\mu\Rightarrow$ K-G becomes $\left[\left(\partial_\mu+\frac{iq}{\hbar}A_\mu\right)\left(\partial^\mu+\frac{iq}{\hbar}A^\mu\right)+\left(\frac{mc}{\hbar}\right)^2\right]\psi(\mathbf{r},t)=0$. Expansion gives $\left[(\hat{\mathbf{p}}-q\mathbf{A})^2c^2+\left(mc^2+S(\mathbf{r})\right)^2\right]\psi(\mathbf{r},t)=\left(i\hbar\partial_t-q\Phi\right)^2\psi(\mathbf{r},t)$. The four-current $j^\mu=i\hbar c\left[\psi^*\left(\partial^\mu+\frac{iq}{\hbar}A^\mu\right)\psi-\psi\left(\partial^\mu-\frac{iq}{\hbar}A^\mu\right)\psi^*\right]$.

Klein paradox. A spinless particle of charge e and energy E_p is incident from the left upon a 1D electrostatic potential $e\Phi(x)=V(x)=\begin{cases}0, & x<0\\ V_0>0, & x>0\end{cases}$. Setting $S=0,\mathbf{A}=0$, K-G gives $\left(-\hbar^2c^2\frac{\partial^2}{\partial x^2}+m^2c^4\right)\psi(x,t)=\left(i\hbar\frac{\partial}{\partial t}-V(x)\right)^2\psi(x,t)$. Let $\psi(x,t)=\phi(x)e^{-iE_pt/\hbar}\Rightarrow$ Stationary equation $\left[\left(E_p-V(x)\right)^2+\hbar^2c^2\frac{\partial^2}{\partial x^2}-m^2c^4\right]\phi(x)=0$. At left, set $\phi_\text{I}(x)=\phi_\text{i}(x)+\phi_\text{r}(x)$, $\phi_\text{i}(x)=Ae^{ipx/\hbar}$, $\phi_\text{r}(x)=Be^{-ipx/\hbar}$. $V(x)=0\Rightarrow p^2=\frac{E_p^2-m^2c^4}{c^2}$. At right $\phi_\text{II}(x)=\phi_\text{t}(x)=Ce^{ip'x/\hbar}\Rightarrow p'^2=\frac{(E_p-V_0)^2-m^2c^4}{c^2}$. Continuity gives $B=\frac{p-p'}{p+p'}A$, $C=\frac{2p}{p+p'}A$. The current $j_\text{i}=2c|A|^2p$, $j_\text{r}=-2c|B|^2p$. Reflection probability $R=-\frac{j_r}{j_i}=\left|\frac{p-p'}{p+p'}\right|^2$. If $E_p>V_0+mc^2$, then $p'\in\mathbb{R}$, $j_\text{t}=2c|C|^2p'\Rightarrow j_\text{t}=j_\text{i}+j_\text{r}$. Transmission probability $T=\frac{j_\text{t}}{j_\text{i}}=1-R$. If $E_p\in\left(V_0-mc^2,V_0+mc^2\right)$, then p' is imaginary. $\phi_\text{t}=Ce^{-|p'|x/\hbar}\Rightarrow$ exponential decay. If $E_p<V_0-mc^2$ then $p'\in\mathbb{R}$. The propagation is allowed even the kinetic energy is below the barrier. $v_g=\frac{\partial E_p}{\partial p'}=-\frac{c^2p'}{V_0-E_p}$. If the wave is moving to the right, $p'<0\Rightarrow R>1$ and $T<0$, $\rho=2(E_p-V_0)|C|^2<0$. Interpretation: All particles coming from the left are totally reflected. For a strong enough potential, particle-antiparticle pairs are created with particles moving to the left ($R>1$) and antiparticles moving to the right ($T<0$).

Central potentials. Assume $\mathbf{A}=0$ and $V(r)=q\Phi(r)$. Take $\psi(\mathbf{r},t)=\phi(\mathbf{r})e^{-iEt/\hbar}$. K–G gives $\left[(E-V(r))^2+\hbar^2c^2\nabla^2-m^2c^4\right]\phi(\mathbf{r})=0$. Let $\nabla^2=\frac{1}{r}\frac{\partial^2}{\partial r^2}r-\frac{\hat{\mathbf{L}}^2}{\hbar^2r^2}$ and $\phi(\mathbf{r})=R_l(r)Y_{l,m}(\theta,\phi)$, where $\hat{\mathbf{L}}^2Y=\hbar^2l(l+1)Y\Longrightarrow$ Radial K-G $\left[\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r-\frac{l(l+1)}{r^2}+k^2\right]R_l(r)=0$, where $k^2=\frac{(E-V(r))^2-m^2c^4}{\hbar^2c^2}$. Let $R_l(r)=\frac{u_l(r)}{r}\Rightarrow\left[\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}+k^2\right]u_l(r)=0$ with $u_l(0)=0$. In an infinite well of radius R. Inside the well $V(r)=0\Rightarrow k_0^2=\frac{E^2-m^2c^4}{\hbar^2c^2}$. For $l=0$, $\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+k_0\right]u(r)=0$, $u(0)=u(R)=0$ gives $u(r)=rR(r)=c_n\sin\frac{n\pi r}{R}$.

K-G atoms. $V(r)=-\frac{Z\alpha\hbar c}{r}$. $\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l(l+1)-(Z\alpha)^2}{r^2}+\frac{2EZ\alpha}{\hbar cr}+\frac{1}{\hbar^2}\left(\frac{E^2}{c^2}-m^2c^2\right)\right]u_l(r)=0$. Let $m'=\frac{E}{c^2}$, $2m'E'=\frac{E^2}{c^2}-m^2c^2$, $l'(l'+1)=l(l+1)-(Z\alpha)^2\Rightarrow\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l'(l'+1)}{r^2}+\frac{2m'Z\alpha c}{\hbar r}+\frac{2m'E'}{\hbar^2}\right]u_l(r)=0\Rightarrow\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{l'(l'+1)}{r^2}-\frac{2m'Z\alpha c}{\hbar r}\right]u_l(r)=\frac{2m'E'}{\hbar^2}u_l(r)$

Dirac equation. $H=c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta mc^2$, compare with $E^2=c^2\mathbf{p}^2+m^2c^4\Rightarrow\{\alpha_i,\alpha_j\}=2\delta_{ij}$, $\{\alpha_i,\beta\}=0$, $\beta^2=1$, $\alpha_i^2=1\to\alpha_i,\beta$ are unitary matrices with eigenvalue ±1. Consider $\alpha_i\beta+\beta\alpha_i=0\Rightarrow\mathrm{Tr}(\beta)=\mathrm{Tr}(\alpha_i)=0\Rightarrow$ even dimension. Dirac representation: $\boldsymbol{\alpha}=\begin{pmatrix}0&\boldsymbol{\sigma}\\\boldsymbol{\sigma}&0\end{pmatrix}$, $\beta=\begin{pmatrix}I_2&0\\0&-I_2\end{pmatrix}=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}$. $\alpha_1=\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}$, $\alpha_2=\begin{pmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{pmatrix}$, $\alpha_3=\begin{pmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{pmatrix}$. $\psi(\mathbf{r},t)=\begin{pmatrix}\psi_1(\mathbf{r},t)\\\psi_2(\mathbf{r},t)\\\psi_3(\mathbf{r},t)\\\psi_4(\mathbf{r},t)\end{pmatrix}$.

Dirac equation $i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)=\left(c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}+\beta mc^2\right)\psi(\mathbf{r},t)=\left(-i\hbar c\boldsymbol{\alpha}\cdot\nabla+\beta mc^2\right)\psi(\mathbf{r},t)$. $\psi(\mathbf{r},t)$ has four components. Continuity equation $i\hbar\frac{\partial}{\partial t}\left(\psi^\dagger\psi\right)=-i\hbar c\nabla\cdot\left(\psi^\dagger\boldsymbol{\alpha}\psi\right)\Rightarrow\rho=\psi^\dagger\psi$, $\mathbf{j}=c\psi^\dagger\boldsymbol{\alpha}\psi$. Orbital angular momentum $[\hat{H},\hat{\mathbf{L}}]=-i\hbar c\boldsymbol{\alpha}\times\hat{\mathbf{p}}\neq0$. Consider $\boldsymbol{\Sigma}=\begin{pmatrix}\boldsymbol{\sigma}&0\\0&\boldsymbol{\sigma}\end{pmatrix}$. $[\alpha_i,\Sigma_j]=2i\sum_k\epsilon_{ijk}\alpha_k$, $[\beta,\Sigma_j]=0$. $[\hat{H},\boldsymbol{\Sigma}]=2ic\boldsymbol{\alpha}\times\hat{\mathbf{p}}$. Define $\hat{\mathbf{J}}=\hat{\mathbf{L}}+\frac{\hbar}{2}\boldsymbol{\Sigma}=\hat{\mathbf{L}}+\hat{\mathbf{S}}\Rightarrow[\hat{H},\hat{\mathbf{J}}]=0$. $\left[\hat{S}_i,\hat{S}_j\right]=i\hbar\sum_k\epsilon_{ijk}\hat{S}_k$.

Plane wave solutions $\psi(\mathbf{r},t)=Nu(\mathbf{p})e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}=Nu(\mathbf{p})e^{-ip\cdot r/\hbar}$, where $p\cdot r=p^\mu r_\mu$. Write $u(\mathbf{p})=\begin{pmatrix}\phi\\\chi\end{pmatrix}$, ϕ and χ are 2-spinors. Substitute in K-G: $E\begin{pmatrix}\phi\\\chi\end{pmatrix}=\begin{pmatrix}mc^2I_2&c\boldsymbol{\sigma}\cdot\mathbf{p}\\c\boldsymbol{\sigma}\cdot\mathbf{p}&-mc^2I_2\end{pmatrix}\begin{pmatrix}\phi\\\chi\end{pmatrix}\Rightarrow\begin{cases}\left(E-mc^2\right)\phi=c\boldsymbol{\sigma}\cdot\mathbf{p}\chi\\\left(E+mc^2\right)\chi=c\boldsymbol{\sigma}\cdot\mathbf{p}\phi\end{cases}$. $\chi=\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E+mc^2}\phi$, $E^2\phi=\left(m^2c^4+c^2\mathbf{p}^2\right)\phi$. Positive energy

solution. Take $\phi_1=\begin{pmatrix}1\\0\end{pmatrix}$, $\phi_2=\begin{pmatrix}0\\1\end{pmatrix}$. $u_s(\mathbf{p})=\sqrt{E+mc^2}\begin{pmatrix}\phi_s\\ \frac{c\sigma\cdot\mathbf{p}}{E+mc^2}\phi_s\end{pmatrix}$, $\left|u_s(\mathbf{p})\right|^2=2E$. Normalised $\psi^{(+)}_{\mathbf{p},s}(\mathbf{r},t)=\frac{1}{\sqrt{2EV}}u_s(\mathbf{p})e^{-ip\cdot r/\hbar}$. Negative energy solution. $\psi^{(-)}_{\mathbf{p},s}(\mathbf{r},t)=Nv_s(\mathbf{p})e^{ip\cdot r/\hbar}$, $v(\mathbf{p})=\begin{pmatrix}\phi\\ \chi\end{pmatrix}\Rightarrow\begin{cases}\left(-E-mc^2\right)\phi=-c\boldsymbol{\sigma}\cdot\mathbf{p}\chi\\ \left(-E+mc^2\right)\chi=-c\boldsymbol{\sigma}\cdot\mathbf{p}\phi\end{cases}\Rightarrow\phi=\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E+mc^2}\chi$, $E^2\chi=\left(m^2c^4+c^2\mathbf{p}^2\right)\chi$.
Take $\chi_1=\begin{pmatrix}0\\1\end{pmatrix}$, $\chi_2=\begin{pmatrix}1\\0\end{pmatrix}$. $\psi^{(-)}_{\mathbf{p},s}(\mathbf{r},t)=\frac{1}{\sqrt{2EV}}v_s(\mathbf{p})e^{ip\cdot r/\hbar}$ with $v_s(\mathbf{p})=\sqrt{E+mc^2}\begin{pmatrix}\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E+mc^2}\chi_s\\ \chi_s\end{pmatrix}$ describing a particle with $-\mathbf{p}$ and $E<0$.
General solution $\psi(\mathbf{r},t)=\sum_s a_s u_s(\mathbf{p})e^{-ip\cdot r/\hbar}+\sum_s b_s v_s(\mathbf{p})e^{ip\cdot r/\hbar}$.

Non-relativistic limit. Let $\mathbf{p}\to0$. $u_1(0)=\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$, $u_2(0)=\begin{pmatrix}0\\1\\0\\0\end{pmatrix}$, $v_1(0)=\begin{pmatrix}0\\0\\0\\1\end{pmatrix}$, $v_2(0)=\begin{pmatrix}0\\0\\1\\0\end{pmatrix}$. u_1,v_2 have eigenvalues $\frac{\hbar}{2}$ for $\hat{S}_z=\frac{\hbar}{2}\begin{pmatrix}\sigma_z&0\\0&\sigma_z\end{pmatrix}$ so are considered to have spin-up. u_2,v_1 have spin-down.

Relativistic spin-1/2 particles coupling with EM fields. Minimal coupling $i\hbar\frac{\partial\psi}{\partial t}=c\boldsymbol{\alpha}\cdot(-i\hbar\nabla-q\mathbf{A})\psi+q\Phi\psi+\beta mc^2\psi$ or $\left[\boldsymbol{\alpha}\cdot(\hat{\mathbf{p}}-q\mathbf{A})c+\beta\left(mc^2+S\right)\right]\psi=\left(i\hbar\partial_t-q\Phi\right)\psi$. Consider positive energy solutions $\psi(\mathbf{r},t)=\begin{pmatrix}\phi(\mathbf{r})\\ \chi(\mathbf{r})\end{pmatrix}e^{-iEt/\hbar}$.
Substitution $\begin{cases}i\hbar\frac{\partial\phi}{\partial t}=E\phi=c\boldsymbol{\sigma}\cdot(-i\hbar\nabla-q\mathbf{A})\chi+\left(q\Phi+mc^2\right)\phi\\ i\hbar\frac{\partial\chi}{\partial t}=E\chi=c\boldsymbol{\sigma}\cdot(-i\hbar\nabla-q\mathbf{A})\phi+\left(q\Phi-mc^2\right)\chi\end{cases}\Rightarrow\left(E+mc^2-q\Phi\right)\chi=c\boldsymbol{\sigma}\cdot(-i\hbar\nabla-q\mathbf{A})\phi$. $E\approx mc^2$, $\left|q\Phi\right|\ll2mc^2\Rightarrow$
$\chi\approx\frac{1}{2mc}\boldsymbol{\sigma}\cdot(-i\hbar\nabla-q\mathbf{A})\phi$. $\left|\frac{\chi}{\phi}\right|\sim\frac{mv}{2mc}\sim\frac{v}{c}$. Insert χ gives $i\hbar\frac{\partial\phi}{\partial t}\approx\frac{1}{2m}[\boldsymbol{\sigma}\cdot(-i\hbar\nabla-q\mathbf{A})]^2\phi+\left(q\Phi+mc^2\right)\phi=\left[\frac{(\boldsymbol{\sigma}\cdot(\hat{\mathbf{p}}-q\mathbf{A}))^2}{2m}+\left(q\Phi+mc^2\right)\right]\phi$.
Write $i\hbar\frac{\partial\phi}{\partial t}=\left[\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}-\frac{\hbar q}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}+\left(q\Phi+mc^2\right)\right]\phi=\left[\frac{(\hat{\mathbf{p}}-q\mathbf{A})^2}{2m}-\frac{g_eq}{2m}\hat{\mathbf{S}}\cdot\mathbf{B}+\left(q\Phi+mc^2\right)\right]\phi$. The Dirac equation reduces to the Pauli-Schrodinger equation in the non-relativistic limit.

Probability current of Dirac equation.
$i\hbar\frac{\partial}{\partial t}\psi=-i\hbar c\boldsymbol{\alpha}\cdot\nabla\psi+mc^2\beta\psi\xrightarrow{\psi^\dagger\cdot\text{ equation}}i\hbar\psi^\dagger\frac{\partial}{\partial t}\psi=-i\hbar c\psi^\dagger\boldsymbol{\alpha}\cdot\nabla\psi+mc^2\psi^\dagger\beta\psi=-i\hbar c\psi^\dagger\nabla\cdot(\boldsymbol{\alpha}\psi)+mc^2\psi^\dagger\beta\psi$. (1)
$-i\hbar\frac{\partial}{\partial t}\psi^\dagger=i\hbar c\nabla\psi^\dagger\cdot\boldsymbol{\alpha}+mc^2\psi^\dagger\beta\xrightarrow{\text{equation}\cdot\psi}-i\hbar\left(\frac{\partial}{\partial t}\psi^\dagger\right)\psi=i\hbar c\nabla\psi^\dagger\cdot\boldsymbol{\alpha}\psi+mc^2\psi^\dagger\beta\psi$. (2)
(1) − (2): $i\hbar\frac{\partial}{\partial t}\left(\psi\psi^\dagger\right)=-i\hbar c\left[\psi^\dagger\nabla\cdot(\boldsymbol{\alpha}\psi)+\nabla\psi^\dagger\cdot\boldsymbol{\alpha}\psi\right]=-i\hbar c\nabla\cdot\left(\psi^\dagger\boldsymbol{\alpha}\psi\right)$. $\quad\nabla\cdot(\psi\mathbf{A})=\psi\nabla\cdot\mathbf{A}+\nabla\psi\cdot\mathbf{A}$

Levi-Civita. $\mathbf{c}=\mathbf{a}\times\mathbf{b}\Rightarrow c_i=\sum_{j,k}\epsilon_{ijk}a_jb_k$. $\quad\sum_i\epsilon_{ijk}\epsilon_{imn}=\delta_{jm}\delta_{kn}-\delta_{jn}\delta_{km}$. $\quad[\hat{L}_i,\hat{L}_j]=i\epsilon_{ijk}\hbar\hat{L}_k$.

Pauli matrices. $\sigma_1=\begin{pmatrix}0&1\\1&0\end{pmatrix}$, $\quad\sigma_2=\begin{pmatrix}0&-i\\i&0\end{pmatrix}$, $\quad\sigma_3=\begin{pmatrix}1&0\\0&-1\end{pmatrix}$. $\quad[\sigma_i,\sigma_j]=2i\epsilon_{ijk}\sigma_k$. $\quad\sigma_i\sigma_j=\delta_{ij}I+i\sum_k\epsilon_{ijk}\sigma_k$.
$(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2=\hat{\mathbf{p}}^2I$. $(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2=\sum_{i,j}\sigma_i\hat{p}_i\sigma_j\hat{p}_j=\sum_{i,j}\left(\delta_{ij}I+i\sum_k\epsilon_{ijk}\sigma_k\right)\hat{p}_i\hat{p}_j=\hat{\mathbf{p}}^2I+i\sum_k\sigma_k\sum_{i,j}\epsilon_{kij}\hat{p}_i\hat{p}_j=\hat{\mathbf{p}}^2I+i\sum\sigma_k\left(\hat{\mathbf{p}}\times\hat{\mathbf{p}}\right)_k=\hat{\mathbf{p}}^2I$.
$(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b})=(\mathbf{a}\cdot\mathbf{b})I_2+i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})$.
$[\hat{H},\hat{\mathbf{L}}]=-i\hbar c\boldsymbol{\alpha}\times\hat{\mathbf{p}}$. $\quad\hat{H}=c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}+\beta mc^2$. $[\hat{H},\hat{\mathbf{L}}]=[c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\hat{\mathbf{L}}]=[c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\hat{L}_x]\hat{\mathbf{x}}+[c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\hat{L}_y]\hat{\mathbf{y}}+[c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\hat{L}_z]\hat{\mathbf{z}}$. $\quad\hat{L}_x=y\hat{p}_z-z\hat{p}_y$.
$[\alpha_i,\Sigma_j]=2i\sum_k\epsilon_{ijk}\alpha_k$. $[\alpha_i,\Sigma_j]=\begin{pmatrix}0&\sigma_i\\\sigma_i&0\end{pmatrix}\begin{pmatrix}\sigma_j&0\\0&\sigma_j\end{pmatrix}-\begin{pmatrix}\sigma_j&0\\0&\sigma_j\end{pmatrix}\begin{pmatrix}0&\sigma_i\\\sigma_i&0\end{pmatrix}=\begin{pmatrix}0&\sigma_i\sigma_j-\sigma_j\sigma_i\\\sigma_i\sigma_j-\sigma_j\sigma_i&0\end{pmatrix}=2i\sum_k\epsilon_{ijk}\alpha_k$.
$[\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\hat{L}_x]=[\alpha_x\hat{p}_x+\alpha_y\hat{p}_y+\alpha_z\hat{p}_z,y\hat{p}_z-z\hat{p}_y]=[\alpha_y\hat{p}_y,y\hat{p}_z]-[\alpha_z\hat{p}_z,z\hat{p}_y]=\alpha_y[\hat{p}_y,y]\hat{p}_z-\alpha_z[\hat{p}_z,z]\hat{p}_y=-i\hbar\left(\alpha_y\hat{p}_z-\alpha_z\hat{p}_y\right)$.
$[\hat{H},\hat{\mathbf{S}}]=i\hbar c\boldsymbol{\alpha}\times\hat{\mathbf{p}}$. $\quad\hat{\mathbf{S}}=\frac{\hbar}{2}\boldsymbol{\Sigma}$. Consider $[\boldsymbol{\alpha}\cdot\hat{\mathbf{p}},\Sigma_x]=[\alpha_x\hat{p}_x+\alpha_y\hat{p}_y+\alpha_z\hat{p}_z,\Sigma_x]=[\alpha_y,\Sigma_x]\hat{p}_y+[\alpha_z,\Sigma_x]\hat{p}_z=-2i\alpha_z\hat{p}_y+2i\alpha_y\hat{p}_z=2i\left(\alpha_y\hat{p}_z-\alpha_z\hat{p}_y\right)$.
$\hat{H}=c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}+\beta mc^2+V(r)$. $[V(r),\hat{L}_x]=[V(r),y\hat{p}_z-z\hat{p}_y]=[V(r),\hat{p}_z]y-[V(r),\hat{p}_y]z$.
$[V(r),\hat{p}_z]\psi=V(r)\hat{p}_z\psi-\hat{p}_zV(r)\psi=V(r)\left(-i\hbar\frac{\partial}{\partial z}\psi\right)+i\hbar\frac{\partial}{\partial z}\left(V(r)\psi\right)=i\hbar\left[-V(r)\frac{\partial}{\partial z}\psi+V(r)\frac{\partial}{\partial z}\psi+\psi\frac{\partial}{\partial z}V(r)\right]=i\hbar\psi\frac{\partial V(r)}{\partial z}$.
$\Rightarrow[V(r),\hat{p}_z]=i\hbar\frac{\partial V(r)}{\partial z}=i\hbar\frac{\partial V(r)}{\partial r}\frac{\partial r}{\partial z}=\frac{i\hbar z}{r}\frac{\partial V(r)}{\partial r}$. $[V(r),\hat{L}_x]=\frac{i\hbar(yz-zy)}{r}\frac{\partial V(r)}{\partial r}=0\Rightarrow[V(r),\hat{\mathbf{L}}]=0$.

1. A one-dimensional harmonic oscillator of mass m and angular frequency ω in its ground state is subject to a small force $F=F_0e^{-t/\tau}$ for $t>0$. Find the probability, in the first-order approximation, that the oscillator is in its first excited state in the limit $t\to\infty$.
$\hat{V}(t)=-\Theta(t)F_0e^{-t/\tau}x$. $c^{(1)}=-\frac{i}{\hbar}\int_0^\infty\mathrm{d}t'e^{i\omega_{fi}t'}\langle1|\hat{V}(t)|0\rangle=\frac{i}{\hbar}\int_0^\infty\mathrm{d}t'e^{i\omega_{fi}t'}F_0e^{-t'/\tau}\langle1|x|0\rangle=\frac{iF_0}{\hbar}\langle1|x|0\rangle\int_0^\infty\mathrm{d}t'e^{(i\omega_{fi}-1/\tau)t'}$.
$\phi_0(x)=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$, $\quad\phi_1(x)=\sqrt{\frac{2m\omega}{\hbar}}x\phi_0(x)$. $\langle1|x|0\rangle=\int_{-\infty}^\infty\sqrt{\frac{2m\omega}{\hbar}}x^2\phi_0^2(x)\mathrm{d}x=\sqrt{\frac{2m\omega}{\hbar}}\sqrt{\frac{m\omega}{\pi\hbar}}\int_{-\infty}^\infty x^2\exp\left(-\frac{m\omega x^2}{\hbar}\right)\mathrm{d}x$
$=\sqrt{\frac{2}{\pi}\frac{m\omega}{\hbar}}\int_{-\infty}^\infty x^2\exp(-\alpha x^2)\mathrm{d}x=\sqrt{\frac{2}{\pi}}\alpha\cdot\frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}=\frac{1}{2}\sqrt{\frac{2}{\alpha}}=\sqrt{\frac{\hbar}{2m\omega}}$. $c^{(1)}(\infty)=\frac{iF_0}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\frac{1}{i\omega_{fi}-1/\tau}e^{(i\omega_{fi}-1/\tau)t'}\Big|_0^\infty=iF_0\sqrt{\frac{1}{2m\omega\hbar}}\frac{1}{1/\tau-i\omega_{fi}}$.
$\left|c^{(1)}(\infty)\right|^2=\frac{F_0^2}{2m\omega\hbar}\frac{1}{1/\tau^2+\omega^2}$

Invariance under small translations. $\int \mathrm{d}r\psi_n^*(\mathbf{r})\hat{O}\psi_m(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\psi_n^*(\mathbf{r}-\boldsymbol{\varepsilon})\hat{O}\psi_m(\mathbf{r}-\boldsymbol{\varepsilon}) \approx \int \mathrm{d}r\psi_n^*(\mathbf{r})\left(1+\frac{i}{\hbar}\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}\right)\hat{O}\left(1-\frac{i}{\hbar}\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}\right)\psi_m(\mathbf{r}) \approx \int \mathrm{d}r\psi_n^*(\mathbf{r})\hat{O}\psi_m(\mathbf{r}) + \frac{i}{\hbar}\int \mathrm{d}r\psi_n^*(\mathbf{r})(\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}\hat{O}-\hat{O}\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}})\psi_m(\mathbf{r}) = \int \mathrm{d}r\psi_n^*(\mathbf{r})\hat{O}\psi_m(\mathbf{r}) + \frac{i}{\hbar}\sum_i \varepsilon_i \int \mathrm{d}r\psi_n^*(\mathbf{r})\left(\hat{p}_i\hat{O}-\hat{O}\hat{p}_i\right)\psi_m(\mathbf{r}) \Rightarrow [\hat{p}_i,\hat{O}] = 0.$

Rotations. $\hat{R}_z(\delta\theta) = I - \delta\theta S_3$. $\psi(\mathbf{r}) \to \hat{R}_z\psi(\mathbf{r}) = \psi(R_z(\delta\theta)\mathbf{r}) = \psi(\mathbf{r}-\delta\theta S_3\mathbf{r}) \approx \psi(\mathbf{r}) - \delta\theta S_3\mathbf{r}\cdot\nabla\psi(\mathbf{r})$. $S_3\mathbf{r}\cdot\nabla = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}\cdot\begin{pmatrix} \partial_x \\ \partial_y \\ \partial_z \end{pmatrix} = y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} = -\frac{i}{\hbar}\hat{L}_z$. $R_x(\delta\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\delta\theta & -\sin\delta\theta \\ 0 & \sin\delta\theta & \cos\delta\theta \end{pmatrix}$. $R_y(\delta\theta) = \begin{pmatrix} \cos\delta\theta & 0 & \sin\delta\theta \\ 0 & 1 & 0 \\ -\sin\delta\theta & 0 & \cos\delta\theta \end{pmatrix}$. $R_z(\delta\theta) = \begin{pmatrix} \cos\delta\theta & -\sin\delta\theta & 0 \\ \sin\delta\theta & \cos\delta\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Parity. $\langle\phi|\hat{\mathbf{r}}|\psi\rangle = \int \mathrm{d}r\phi^*(\mathbf{r})\mathbf{r}\psi(\mathbf{r}) \xrightarrow[\text{trans.}]{\text{Parity}} \int \mathrm{d}r\phi^*(-\mathbf{r})\mathbf{r}\psi(-\mathbf{r}) \overset{\mathbf{r}\to-\mathbf{r}}{=\!=\!=} -\int \mathrm{d}r\phi^*(\mathbf{r})\mathbf{r}\psi(\mathbf{r})$. $\hat{P}^\dagger\hat{\mathbf{r}}\hat{P} = -\hat{\mathbf{r}}$.

Transitions. $(2s)^2(2p)(3d)\ {}^3D \to (2s)^2(2p)^2\ {}^3P$. $\Delta L = -1$, $\Delta S = 0$, $P_i = (-1)(-1)^2 = -1, P_f = (-1)^2 = 1$. Allowed.
$(2s)^2(2p)(3s)\ {}^3P \to (2s)^2(2p)^2\ {}^1S$. $\Delta S \neq 0$. Forbidden. $(2s)^2(2p)(3d)\ {}^1D \to (2s)^2(2p)(3s)\ {}^1P$. $P_i = P_f$. Forbidden.
$(2s)(2p)^3\ {}^3D \to (2s)^2(2p)^2\ {}^3P$. $P_i = (-1)^3 = -1$, $P_f = (-1)^2 = 1$, $\Delta L = -1$, $\Delta S = 0$. Allowed.
$(2s)^2(2p)(3p)\ {}^3P \to (2s)^2(2p)^2\ {}^3P$. $P_i = (-1)^2 = P_f = (-1)^2$. Forbidden. $(2s)^2(2p)(3d)\ {}^1D \to (2s)^2(2p)^2\ {}^1S$. $\Delta L = 2$. Forbidden.