University of Illinois at Chicago
Department of Physics

Quantum Mechanics
Qualifying Examination

January 7, 2013 (Tuesday)
9:00 am - 12:00 noon

Full credit can be achieved from completely correct answers to **4 questions**. If the student attempts all 5 questions, all of the answers will be graded, and the **top 4 scores** will be counted toward the exam's total score.

Formulas

$$\int_0^\infty x^n e^{-ax} dx = n!/a^{n+1} \ , \quad \text{valid for complex } a \text{ as long as } \mathrm{Re}(a) > 0.$$

$$\int_{-\infty}^\infty e^{-\lambda x^2} dx = \sqrt{\pi/\lambda} \ , \quad \text{valid for complex } a \text{ as long as } \mathrm{Re}(\lambda) \geq 0.$$

$$\int_{-\infty}^\infty x^2 e^{-\lambda x^2} dx = \frac{1}{2\lambda}\sqrt{\frac{\pi}{\lambda}} \ , \quad \frac{\int_{-\infty}^\infty x^2 e^{-\lambda x^2} dx}{\int_{-\infty}^\infty e^{-\lambda x^2} dx} = \frac{1}{2\lambda} \ .$$

$$\text{Fourier transform: } \tilde{\psi}(k) = \tfrac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{-ikx} \psi(x) dx \ , \ \tilde{\psi}(x) = \tfrac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \psi(k) e^{ikx} dk \ .$$

$$\langle \mathcal{O} \rangle = \int\int\int \Psi^*(\boldsymbol{x}) \mathcal{O} \Psi(\boldsymbol{x}) d^3x \ .$$

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

$$\sigma_x\sigma_y = i\sigma_z = -\sigma_y\sigma_x \ , \sigma_y\sigma_z = i\sigma_x = -\sigma_z\sigma_y \ , \sigma_z\sigma_x = i\sigma_y = -\sigma_x\sigma_z \ .$$

(1) **Gaussian Wave Packet**

A Gaussian wave packet describes the initial amplitude of a free non-relativistic one-dimensional quantum particle of mass $m = \frac{1}{2}$ (in units $\hbar = 1$),

$$\psi(x, t = 0) = N \exp(-3x^2 + 5x + i100x) \ .$$

(a) By completing the square of the **real** part of the exponent, determine the wave function normalization factor N.

(b) Find the mean position $\langle x \rangle$ and the mean wave number $\langle p \rangle$ of the particle.

(c) What is the wave-number amplitude $\tilde{\psi}(k)$ in the wave-number k-representation (or the momentum representation)?

(d) Find the uncertainties of the position and the momentum, $\sqrt{\langle (x - \langle x \rangle)^2 \rangle}$, $\sqrt{\langle (p - \langle p \rangle)^2 \rangle}$,

(e) What is the group velocity of the packet?

(f) How is this wave-number amplitude $\tilde{\psi}$ changed in time?

(g) Find $\psi(x, t)$. Your result can be in an integral form. Describe qualitatively how the wave function evolves.

By completing the square for the real part of the exponent, we derive

$$\psi(x, 0) = N \exp\left(-3(x - \tfrac{5}{6})^2 + \tfrac{25}{12} + i100x\right) \ .$$

It is easy to claim $\langle x \rangle = \frac{5}{6}$. The Gaussian integral gives

$$1/N^2 = \int_{-\infty}^{\infty} e^{-6(x-\frac{5}{6})^2} dx e^{\frac{25}{6}} \ , \ N = e^{-\frac{25}{12}} \left(\tfrac{6}{\pi}\right)^{\frac{1}{4}} \ .$$

$$\psi(x, 0) = \left(\tfrac{6}{\pi}\right)^{\frac{1}{4}} e^{i\frac{500}{6}} \exp\left(-3(x - \tfrac{5}{6})^2 + i100(x - \tfrac{5}{6})\right) \ .$$

Let $x' = x - \frac{5}{6}$ be the new coordinate. Then in primed variables,

$$\psi'(x', 0) = \left(\tfrac{6}{\pi}\right)^{\frac{1}{4}} e^{i\frac{500}{6}} \exp\left(-3x'^2 + i100x'\right) \ .$$

However, the physics is just a translation, so we drop the primes unless we specify the variables of the original coordinate.

Therefore, $\boxed{\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x, 0) x \psi(x, 0) dx = 0}$ in the translated coordinate. The Gaussian standard deviation gives $\boxed{\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x, 0) x^2 \psi(x, 0) dx = \frac{1}{2} \frac{1}{6} = \frac{1}{12}}$.

The Fourier analysis gives the wave amplitude in the momentum representation,

$$\tilde{\psi}(k) = \tfrac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x, 0) e^{-ikx} dx = \underbrace{\left(\tfrac{6}{\pi}\right)^{\frac{1}{4}} e^{i\frac{500}{6}} \tfrac{1}{\sqrt{2\pi}}}_{C} \int_{-\infty}^{\infty} e^{-3x^2 - (k-100)ix} dx \ .$$

The exponent in the integrand can be in the complete square form, which is

$$-3(x + \tfrac{i}{6}(k-100)^2) - \tfrac{1}{12}(k-100)^2 \quad \text{, and it gives } \tilde{\psi}(k) = C\sqrt{\tfrac{\pi}{3}}e^{-\frac{1}{12}(k-100)^2} \ .$$

It is again a Gaussian, centered at $\langle k \rangle = \langle p \rangle = 100$. The Gaussian standard deviation gives

$$\langle (k-100)^2 \rangle = \tfrac{1}{2}\ 6 = 3 \ , \ \langle (\Delta k)^2 \rangle = 3 \ .$$

Combining earlier result in the position uncertainty, $\langle (\Delta x)^2 \rangle = \frac{1}{12}$, we observe the saturation of the Heisenberg's uncertainty inequality, $\langle (\Delta k)^2 \rangle \langle (\Delta x)^2 \rangle = \frac{1}{4}$,

The time evolution in the momentum representation $\tilde{\psi}$ is simply given by attaching the time-energy factor $e^{-ik^2 t}$ in our units, $2m = 1, \hbar = 1$.

$$\tilde{\psi}(k,t) = C\sqrt{\tfrac{\pi}{3}}e^{-\frac{1}{12}(k-100)^2 - ik^2 t} \ , \ \psi(x,t) = \tfrac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \tilde{\psi}(k,t)e^{+ikx}dk \ .$$

In the narrow Δk approximation, the wave packet travels at the group velocity $\frac{k}{m} = 200$ during the beginning short interval. However, when the time is much longer, the wave will disperse.

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(2) **Hydrogen bound states.**
In units $2m = 1, \hbar = 1$, the radial Schrödinger equation of the hydrogen atom is given by

$$\left[-\tfrac{d^2}{dr^2} - \tfrac{g^2}{r} + \tfrac{\ell(\ell+1)}{r^2}\right] u(r) = \varepsilon u(r) \ .$$

The lowest eigenstate of a given ℓ is known to have the form, $u^0_\ell(r) = C_\ell r^{\ell+1}\exp(-r/a_\ell)$.

(a) For a given ℓ, determine the eigenvalue ε^0_ℓ and the size parameter a_ℓ, in terms of the Coulomb strength g^2.

(b) The initial 3-dimensional wave function at $t = 0$ is the superposition of the above states $\ell = 0, 1$.

$$\psi(x,0) = D\left(e^{-g^2\frac{r}{2}} + g^2 r e^{-g^2\frac{r}{4}}\cos\theta\right) \ .$$

Determine the quantum expectation average of $\langle \cos\theta \rangle$ as a function of time.

$$\tfrac{d}{dr}u^0_\ell(r) = C_\ell[(\ell+1)r^\ell - \tfrac{1}{a_\ell}r^{\ell+1}]\exp(-r/a_\ell) \ ,$$

$$\tfrac{d^2}{dr^2}u^0_\ell(r) = C_\ell[\ell(\ell+1)/r^2 - \tfrac{2}{r}\tfrac{\ell+1}{a_\ell} + \tfrac{1}{a_\ell^2}]r^{\ell+1}\exp(-r/a_\ell) \ .$$

$$\left[-\tfrac{d^2}{dr^2} - \tfrac{2}{r}\tfrac{\ell+1}{a_\ell} + \tfrac{\ell(\ell+1)}{r^2}\right] u^0_\ell(r) = -\tfrac{1}{a_\ell^2}u^0_\ell(r) \ .$$

Comparing it with the Schrödinger equation, we identify the relations,

$$g^2 = (\ell+1)\tfrac{2}{a_\ell} \ , \text{ so the ground state energy is } \quad \epsilon^0_\ell = -\tfrac{1}{a_\ell^2} = -g^4/[2(\ell+1)]^2 \ .$$

Now the initial state is given by

$$\psi(x,0) = D\left(e^{-g^2\frac{r}{2}} + gr^2 e^{-g^2\frac{r}{4}}\cos\theta\right) \ .$$

The first term corresponds to the ground s-wave, and the second one corresponds to the lowest p-wave. Their energies are $-g^4/4$ and $-g^4/16$ respectively.

$$\psi(x,t) = D\left(e^{-g^2\frac{r}{2}+i\frac{g^4}{4}t} + g^2 r e^{-g^2\frac{r}{4}+i\frac{g^4}{16}t}\cos\theta\right) .$$

The normalization can be determined at $t = 0$.

$$1/D^2 = 4\pi\int_0^\infty \left(e^{-g^2 r} + \tfrac{1}{3}g^4 r^2 e^{-\frac{g^2}{2}r}\right) r^2 dr = 4\pi\tfrac{2!}{(g^2)^3}(1+\tfrac{4\cdot 3\cdot 2^5}{3}) = 1032\pi/g^6 .$$

Above, the cross term is understood to be zero. However, the average $\langle\cos\theta\rangle$ is from the cross term,

$$\langle\cos\theta\rangle = 2\tfrac{g^8}{1032\pi}\left(\int_{-1}^{+1}\cos^2\theta d\cos\theta 2\pi\right)\left(\int_0^\infty e^{-\frac{3}{4}g^2 r} r^3 dr\right)\cos(\tfrac{3}{16}g^4 t) .$$

$$\boxed{\langle\cos\theta\rangle = \tfrac{512}{10449}\cos(\tfrac{3}{16}g^4 t)} .$$

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(3) **Planar Rotor and Perturbation.**
A permanent planar dipole $\boldsymbol{p}$, which lies on the x-y plane, is described by the rotation Hamiltonian $H_R = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$, where ϕ is the angle of $\boldsymbol{p}$ with respect to the x axis.

(a) Write down the three lowest energy eigenvalues and their corresponding eigenstates. Arrange these states to be eigenstates of the angular momentum operator $L_z = -i\hbar\frac{d}{d\phi}$.

(b) A weak electric field $\boldsymbol{E}$ along the y axis is turned on. The interaction is given by $-\boldsymbol{p}\cdot\boldsymbol{E}$. Find all matrix elements of this perturbed energy operator between H_R eigenstates in (a). The result is expressed in terms of p,E,$\hbar$ and I.

(c) Determine the perturbed energies to the second order effect for the lowest lying states.

The equation $-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\psi(\phi) = \epsilon\psi(\phi)$ implies the eigenvalues to be quantized as $\epsilon = \frac{\hbar^2 m^2}{2I}$ with the integer magnetic number $m = 0, \pm1, \pm2, \cdots$ because of the periodic condition in the angle ϕ. When we label the eigenstates ψ_m by the m index, they are

$$\psi_0(\phi) = \tfrac{1}{\sqrt{2\pi}} ,\ \psi_{\pm1}(\phi) = \tfrac{1}{\sqrt{2\pi}}e^{\pm i\phi} ,\ \psi_{\pm2}(\phi) = \tfrac{1}{\sqrt{2\pi}}e^{\pm i2\phi} ,\cdots\ \psi_{\pm m}(\phi) = \tfrac{1}{\sqrt{2\pi}}e^{\pm im\phi} ,\cdots .$$

They are also eigenstates of the angular momentum operator L_z, whose eigenvalues are $0, \pm1, \pm2, \cdots, \pm m, \cdots$. Now the perturbed Hamiltonian is $\Delta H = -\boldsymbol{p}\cdot\boldsymbol{E} = -pE\sin\phi$.

$$\langle m'|\Delta H|m\rangle = \tfrac{pE}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\sin\phi d\phi = \tfrac{pE}{2\pi}\tfrac{1}{2i}\int_0^{2\pi}\left[e^{i(m-m'+1)\phi} - e^{i(m-m'-1)\phi}\right] d\phi$$

$$\langle m'|\Delta H|m\rangle = \begin{cases} \frac{pE}{2i} & \text{for } m' = m+1 \ , \\ -\frac{pE}{2i} & \text{for } m' = m-1 \ , \\ 0 & \text{otherwise} \ . \end{cases}$$

The corrected energies up to the second order are

$$E_0 = 0 + 0 - \frac{p^2E^2}{4}\left(\frac{1}{\frac{\hbar^2}{2I}}\right) + \cdots = -\frac{p^2E^2I}{2\hbar^2} + \cdots \ ,$$

$$E_1 = \frac{\hbar^2}{2I} + 0 + \frac{p^2E^2}{4}\left(\frac{1}{\frac{\hbar^2}{2I}} - \frac{1}{\frac{3\hbar^2}{2I}}\right) + \cdots = \frac{\hbar^2}{2I} + \frac{p^2E^2I}{3\hbar^2} + \cdots \ ,$$

$$E_2 = \frac{4\hbar^2}{2I} + 0 + \frac{p^2E^2}{4}\left(\frac{1}{\frac{3\hbar^2}{2I}} - \frac{1}{\frac{5\hbar^2}{2I}}\right) + \cdots = \frac{4\hbar^2}{2I} + \frac{p^2E^2I}{15\hbar^2} + \cdots \ ,$$

Note that the degeneracy relation $E_m = E_{-m}$ still holds.

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(4) **Fermi-Golden rule, scattering length, Born approximation.**
The asymptotic form of a scattering wave is given by $\psi(\boldsymbol{x}) \longrightarrow e^{i\mathbf{k}\cdot\mathbf{x}} + f(\theta)\frac{e^{ikr}}{r}$ for a particle of mass m in a spherical potential $V(r)$. The scattering amplitude is given by the Born approximation for a weak potential,

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'}V(r')d^3\mathbf{r}' \ .$$

(a) Carry out the angular integration in $f(\theta)$ so that only the radial integration remains. Simplify the result in terms of q ($\boldsymbol{q} = \boldsymbol{k'} - \boldsymbol{k}$).

(b) Find the differential cross section $d\sigma/d\Omega = |f(\theta)|^2$ for a weak delta-shell potential $V(r) = g\ \delta(r-R)$, located at the radius R.

(c) On the other hand, the cross-section can be derived from the Fermi Golden Rule about the transition rate from an initial state i to the final states f,

$$\Gamma = \tfrac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\rho(E_f) \ ,$$

where $\rho(E_f)$ counts the final state density when the system is confined in a very large cube with the periodic boundary condition. Derive the Born cross-section result from the Fermi golden rule by working out the state density, the solid angle differential, and the incident flux.

(d) The scattering problem can also be solved by the phase shift method. In the low energy limit of a very small k, the s-wave outside the potential range becomes a straight line $r\psi(r) = u(r) \longrightarrow A\times(r-a)$. Here A is an arbitrary multiplicative constant. The parameter a, i.e. the extrapolated intercept of the outside wave, is called the scattering length. As the s-wave effect dominates at the low k, we know that $f(\theta) \approx -a$.
Determine the scattering length a for the above delta-shell potential, in terms of the shell radius R and the strength g, by solving the corresponding radial Schrödinger equation at $k \approx 0$,

$$-\tfrac{d^2}{dr^2}u(r) + g\delta(r-R)u(r) = 0 \ .$$

Confront your result with Born approximation.

The Born scattering amplitude for a central force is given by

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}V(\boldsymbol{r'})d^3\boldsymbol{r'} = -\frac{m}{2\pi\hbar^2}\int_0^\infty r^2V(r)dr\int_{-1}^{+1}2\pi\ d(\cos\theta)\ e^{iqr\cos\theta}$$

$$= -\frac{m}{\hbar^2}\int_0^\infty \frac{r}{iq}\left[e^{iq}-e^{-iq}\right]V(r)dr = -\frac{2m}{\hbar^2 q}\int_0^\infty r\sin(qr)V(r)dr\ ,$$

where the momentum transfer $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k'}$ and $q = 2k\sin\frac{\theta}{2}$. For the present case that $V(r) = g\delta(r-R)$,

$$f(\theta) = -\frac{2mgR}{\hbar^2 q}\sin qR\ , \quad \frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left(\frac{2mgR}{\hbar^2 q}\right)^2\sin^2 qR\ .$$

The density of state in the Fermi Golden Rule (FGR) is

$$\delta\rho(E)dE = \frac{L^3d^3\mathbf{p}}{(2\pi\hbar)^3} = \frac{L^3 4\pi p^2dp}{(2\pi\hbar)^3}\ , \delta\rho(E)\frac{pdp}{m} = \frac{L^3p^2dp\delta\Omega}{(2\pi\hbar)^3}\ .$$

We have $\boxed{\delta\rho(E) = \frac{L^3mp}{(2\pi\hbar)^3}\delta\Omega}$. Since the transition rate Γ in the FGR, when normalized by the incoming flux ($I = \frac{1}{L^3}\ \frac{p}{m}$), is the cross-section, we obtain

$$\delta\sigma = \frac{\delta\Gamma}{I} = \frac{\frac{2\pi}{\hbar}|\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}V(\boldsymbol{r'})\frac{1}{L^3}d^3\boldsymbol{r'}|^2\frac{L^3mp}{(2\pi\hbar)^3}\delta\Omega}{\frac{1}{L^3}\ \frac{p}{m}}\ .$$

Note that the artificial L^3 factors cancel completely. We obtain the desirable Born formula.

$$\frac{d\sigma}{d\Omega} = \left|\frac{m}{2\pi\hbar^2}\ \int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}V(\boldsymbol{r'})d^3\boldsymbol{r'}\right|^2\ .$$

The 1-d radial solution $u(r)$ at the low energy ($k\to 0$) becomes a straight line,

$$u(r) = \begin{cases} A(r-a) & \text{for } r>R\ ,\ \text{here } a \text{ is the scattering length,} \\ Br & \text{for } r<R\ \text{ because u(0)=0} \end{cases}$$

The continuity of u at $r=R$ relate A and B so that $A(R-a) = BR$. The delta potential gives rise to a kink,

$$-\frac{\hbar^2}{2m}\left[u'(R_>) - u'(R_<)\right] + gu(R) = 0\ , -\frac{\hbar^2}{2m}(A-B) + gA(R-a) = 0\ .$$

Combining the matching conditions, we obtain $\boxed{a = gR/(g+\frac{\hbar^2}{2mR})}$. The result is in agreement with the Born approximation for a weak coupling $g\to 0$ at the very low energy $k\to 0$, where $f(\theta) = -a$.

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(5) **Coupled Angular Momenta.**
We study the composite system of two localized spin-half particles, 1 and 2. Their corresponding Pauli matrices are $\sigma_i^{(1)}$ and $\sigma_i^{(2)}$. The spin-spin interaction among them is described by

$$H = \sigma_x^{(1)}\sigma_x^{(2)} + \sigma_y^{(1)}\sigma_y^{(2)} + \sigma_z^{(1)}\sigma_z^{(2)}\ .$$

(a) Find the energy eigenstates and eigenvalues of H, by using the property of the angular momentum sum.

(b) Then find the energy eigenstates and eigenvalues of another Hamiltonian,

$$H^{(+)} = \sigma_y^{(1)}\sigma_y^{(2)} + \sigma_x^{(1)}\sigma_x^{(2)} \ .$$

(c) When the spin state $|\psi\rangle$ of *one* single spin-half particle is rotated about the y-axis by an angle β, the new state $|\psi'\rangle = U|\psi\rangle$ is described by the unitary transformation $U = \exp(-i\sigma_y\beta/2)$.

Work out the explicit entries in the matrix U in terms of β. The Pauli matrices σ_i $(i = x, y, z)$ when transformed becomes $\sigma_i' = U\sigma_i U^\dagger$. Work out the explicit relation that $\sigma_x' = c_1\sigma_x + c_2\sigma_z$ and express the coefficients c_1, c_2 in terms of the angle β. Do the same calculation for σ_z' and σ_y'. Explain the physical meaning of the transformation.

Show the result for the special case of $\beta = \pi$.

(d) Finally, If the relative sign of terms in $H^{(+)}$ is flipped to give the third Hamiltonian,

$$H^{(-)} = \sigma_y^{(1)}\sigma_y^{(2)} - \sigma_x^{(1)}\sigma_x^{(2)} \ .$$

How is $H^{(-)}$ related to $H^{(+)}$ by a unitary transformation? What is the energy eigenstates and eigenvalues of $H^{(-)}$?

$$U(\beta) = e^{-i\beta\sigma_y/2} = \cos\tfrac{\beta}{2} - i\sigma_y \sin\tfrac{\beta}{2} = \begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix} \ .$$

It is easy to see σ_y unchanged after transformation, $U(\beta)\sigma_y U^\dagger(\beta) = \sigma_y$. However,

$$U(\beta)\sigma_x U^\dagger(\beta) = \left(\cos\tfrac{\beta}{2} - i\sigma_y\sin\tfrac{\beta}{2}\right)\sigma_x\left(\cos\tfrac{\beta}{2} + i\sigma_y\sin\tfrac{\beta}{2}\right)$$

$$= \left(\cos^2\tfrac{\beta}{2} - \sin^2\tfrac{\beta}{2}\right)\sigma_x - \left(2\sin\tfrac{\beta}{2}\cos\tfrac{\beta}{2}\right)\sigma_z = \cos\beta\sigma_x - \sin\beta\sigma_z \ .$$

Similarly,

$$U(\beta)\sigma_z U^\dagger(\beta) = \left(\cos\tfrac{\beta}{2} - i\sigma_y\sin\tfrac{\beta}{2}\right)\sigma_z\left(\cos\tfrac{\beta}{2} + i\sigma_y\sin\tfrac{\beta}{2}\right)$$

$$= \left(\cos^2\tfrac{\beta}{2} - \sin^2\tfrac{\beta}{2}\right)\sigma_z + \left(2\sin\tfrac{\beta}{2}\cos\tfrac{\beta}{2}\right)\sigma_x = \cos\beta\sigma_z + \sin\beta\sigma_z \ .$$

Therefore, the 2-component spinor is transformed by the *half-angle* formula. However, the operators are transformed by the whole angle β, like rotating a vector. In summary, $\boxed{\sigma_y' = \sigma_y \ , \ \sigma_x' = \cos\beta\sigma_x - \sin\beta\sigma_z \ , \ \sigma_z' = \sin\beta\sigma_x + \cos\beta\sigma_z}$.

In the special case, $\beta = \pi$, we have $\sigma_y' = \sigma_y \ , \ \sigma_x' = -\sigma_x \ , \ \sigma_z' = -\sigma_z$.

Now we work on the spin-spin coupling in the problem.

$$2H = 2\boldsymbol{\sigma}^{(1)}\cdot\boldsymbol{\sigma}^{(2)} = \left(\boldsymbol{\sigma}^{(1)} + \boldsymbol{\sigma}^{(2)}\right)^2 - \left(\boldsymbol{\sigma}^{(1)}\right)^2 - \left(\boldsymbol{\sigma}^{(2)}\right)^2$$

$$= (2\boldsymbol{S})^2 - \left(2\boldsymbol{s}^{(1)}\right)^2 - \left(2\boldsymbol{s}^{(2)}\right)^2$$

$$= 4S(S+1) - 4\cdot\tfrac{1}{2}\cdot\tfrac{3}{2} - 4\cdot\tfrac{1}{2}\cdot\tfrac{3}{2} \ .$$

The energy eigenvalues for the triplet and the singlet are

$$E_S = 2S(S+1) - 2\cdot\tfrac{1}{2}\cdot\tfrac{3}{2} - 2\cdot\tfrac{1}{2}\cdot\tfrac{3}{2} = \begin{cases} +1 & \text{for the triplet } S=1 \ , \\ -3 & \text{for the singlet } S=0 \ . \end{cases}$$

Now we move to a less symmetric system,

$$H^{(+)} = H - \left(\sigma_z^{(1)}\right)\left(\sigma_z^{(2)}\right) \ , \quad E^{(+)}_{S,S_z} = E_S - \left(\sigma_z^{(1)}\right)\left(\sigma_z^{(2)}\right) \ .$$

Therefore,

$$E^{(+)}_{S,S_z} = \begin{cases} 0 & \text{for the triplet } S=1 \ , \ S_z = \pm 1 \ , \ \uparrow\uparrow \ \text{or} \ \downarrow\downarrow \ , \\ 2 & \text{for the triplet } S=1 \ , \ S_z = 0 \ , \ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \ , \\ \\ -2 & \text{for the singlet } S=0 \ , \ S_z = 0 \ , \ \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \ . \end{cases}$$

The arrows in the first and the second positions represent the state configuration of the first and second spins.

Now we study the last system $H^{(-)}$, which is similar to $H^{(+)}$ with a relative sign flip. The two Hamiltonians are related by a unitary transformation,

$U^{(2)}H^{(-)}U^{(2)\dagger} = H^{(+)}$, where we only rotate the second spin by the angle $\beta = \pi$.

The eigenvalues are unchanged. We obtain

$$E^{(-)}_{S,S_z} = \begin{cases} 0 & \text{for } \uparrow\downarrow \ \text{or} \ \downarrow\uparrow \ , \\ -2 & \text{for } \frac{1}{\sqrt{2}}(\uparrow\uparrow - \downarrow\downarrow) \ , \\ \\ +2 & \text{for } \frac{1}{\sqrt{2}}(\uparrow\uparrow + \downarrow\downarrow) \ . \end{cases}$$
