

## 1. Gauge invariance and the Lorentz force

(a)

Schroedinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right)^2 \psi + q\phi\psi$$

Complex conjugate

$$\begin{aligned} -i\hbar \frac{\partial \psi^*}{\partial t} &= -\frac{\hbar^2}{2m} \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right)^2 \psi^* + q\phi\psi^* \\ i\hbar \psi^* \frac{\partial \psi}{\partial t} &= -\psi^* \frac{\hbar^2}{2m} \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right)^2 \psi + q\phi\psi^*\psi \\ -i\hbar \psi \frac{\partial \psi^*}{\partial t} &= -\frac{\hbar^2}{2m} \psi \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right)^2 \psi^* + q\phi\psi^*\psi \\ i\hbar \frac{\partial \psi^*\psi}{\partial t} &= -\psi^* \frac{\hbar^2}{2m} \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right)^2 \psi + \frac{\hbar^2}{2m} \psi \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right)^2 \psi^* \\ &= -\frac{\hbar^2}{2m} \left( \nabla \left( \psi^* \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right) \psi \right) - \left| \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right) \psi \right|^2 \right) \\ &\quad + \frac{\hbar^2}{2m} \left( \nabla \left( \psi \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right) \psi^* \right) - \left| \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right) \psi \right|^2 \right) \\ &= \frac{\hbar^2}{2m} \nabla \left( \psi \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right) \psi^* - \psi^* \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right) \psi \right) \\ \frac{\partial \rho}{\partial t} &= \frac{\hbar}{2mi} \nabla \left( \psi \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right) \psi^* - \psi^* \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right) \psi \right) \\ &= -\nabla \cdot \vec{j} \\ 0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} \end{aligned}$$

(b)

Under time reversal transformation

$$\begin{aligned} -i\hbar \frac{\partial \psi^*}{\partial t} + \frac{\hbar^2}{2m} \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right)^2 \psi^* - q\phi\psi^* \\ = \frac{\hbar^2}{2m} \left( \left( \nabla - \frac{iq}{\hbar c} \vec{A} \right)^2 - \left( \nabla + \frac{iq}{\hbar c} \vec{A} \right)^2 \right) \psi^* \\ \neq 0 \end{aligned}$$

(c)

Derivatives,

$$\begin{aligned} \frac{\partial L}{\partial \dot{r}_i} &= m\dot{r}_i + \frac{q}{c} A_i \\ \frac{\partial L}{\partial r_i} &= -q\partial_i\phi + \frac{q}{c} \dot{r}_j \partial_i A_j \end{aligned}$$

Euler-Lagrange equation

$$\begin{aligned}
0 &= m\ddot{r}_i + \frac{q}{c} \frac{dA_i}{dt} + q\partial_i\phi - \frac{q}{c} \dot{r}_j \partial_i A_j \\
m\ddot{r}_i &= -\frac{q}{c} \frac{dA_i}{dt} - q\partial_i\phi + \frac{q}{c} \dot{r}_j \partial_i A_j \\
&= -q\partial_i\phi - \frac{q}{c} \partial_t A_i - \frac{q}{c} \dot{r}_j \partial_j A_i + \frac{q}{c} \dot{r}_j \partial_i A_j \\
&= qE_i + \frac{q}{c} (\delta_{ln} \delta_{im} - \delta_{lm} \delta_{in}) \dot{r}_l \partial_m A_n \\
&= qE_i + \frac{q}{c} \varepsilon_{ilj} \dot{r}_l \varepsilon_{jmn} \partial_m A_n \\
&= qE_i + \frac{q}{c} \varepsilon_{ilj} \dot{r}_l B_j \\
&= qE_i + \frac{q}{c} (\vec{v} \times \vec{B})_i
\end{aligned}$$

**2.**

(a)

For each step

$$K(x_{j+1}, x_j; \varepsilon) = \sqrt{\frac{m}{2\pi i \hbar \varepsilon}} \exp\left(\frac{i}{\hbar} (a_1(x_{j+1}^2 + x_j^2) - 2b_1 x_{j+1} x_j)\right)$$

where  $a_1 \equiv \frac{m}{2\varepsilon} \left(1 - 2\left(\frac{\omega\varepsilon}{2}\right)^2\right)$ ,  $b_1 \equiv \frac{m}{2\varepsilon}$ . Assume,

$$\begin{aligned}
&\left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{n/2} \prod_{j=1}^n \int dx_{j-1} \exp\left(\frac{i}{\hbar} \sum_{j=1}^n (a_1(x_{j-1}^2 + x_j^2) - 2b_1 x_{j-1} x_j)\right) \\
&= A_n \exp\left(\frac{i}{\hbar} (a_n(x_n^2 + x_0^2) - 2b_n x_n x_0)\right)
\end{aligned}$$

and  $a_n^2 - b_n^2 = a_1^2 - b_1^2$

$$\begin{aligned}
&A_{n+1} \exp\left(\frac{i}{\hbar} (a_{n+1}(x_0^2 + x_{n+1}^2) - 2b_{n+1} x_0 x_{n+1})\right) \\
&= A_n \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{1/2} \int dx_n \exp\left(\frac{i}{\hbar} (a_1(x_{n+1}^2 + x_n^2) - 2b_1 x_{n+1} x_n + a_n(x_n^2 + x_0^2) - 2b_n x_n x_0)\right) \\
&= A_n \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{1/2} \int dx_n \exp\left(\frac{i}{\hbar} ((a_1 + a_n)x_n^2 - 2(b_1 x_{n+1} + b_n x_0)x_n + a_1 x_{n+1}^2 + a_n x_0^2)\right) \\
&= A_n \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{1/2} \sqrt{\frac{i\pi\hbar}{a_1 + a_n}} \exp\left(\frac{i}{\hbar} \left(-\frac{(b_1 x_{n+1} + b_n x_0)^2}{a_1 + a_n} + a_1 x_{n+1}^2 + a_n x_0^2\right)\right) \\
&= A_n \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{1/2} \sqrt{\frac{i\pi\hbar}{a_1 + a_n}} \exp\left(\frac{i}{\hbar} \left(\left(a_1 - \frac{b_1^2}{a_1 + a_n}\right)(x_{n+1}^2 + x_0^2) - 2\frac{b_1 b_n}{a_1 + a_n} x_{n+1} x_0\right)\right)
\end{aligned}$$

So  $a_{n+1} = a_1 - \frac{b_1^2}{a_1 + a_n}$ ,  $b_{n+1} = \frac{b_1 b_n}{a_1 + a_n}$ , which also satisfy  $a_{n+1}^2 - b_{n+1}^2 = a_1^2 - b_1^2$ . Let  $\frac{\omega\varepsilon}{2} = \sin \frac{\tilde{\omega}\varepsilon}{2}$

$$\begin{aligned} a_1 &= b_1 \cos \tilde{\omega}\varepsilon \\ a_n &= \sqrt{b_n^2 - b_1^2 \sin^2 \tilde{\omega}\varepsilon} \\ \frac{1}{b_{n+1}} &= \frac{\cos \tilde{\omega}\varepsilon + \sqrt{\frac{b_n^2}{b_1^2} - \sin^2 \tilde{\omega}\varepsilon}}{b_n} \\ \frac{1}{b_n} &= \frac{\sin n\tilde{\omega}\varepsilon}{b_1 \sin \tilde{\omega}\varepsilon} \\ a_n &= \frac{m \sin \tilde{\omega}\varepsilon}{2\varepsilon} \frac{\cos n\tilde{\omega}\varepsilon}{\sin n\tilde{\omega}\varepsilon} \end{aligned}$$

In the small  $\varepsilon$  limit and when  $n = N$

$$\begin{aligned} \frac{1}{b} &= \frac{2 \sin \omega t}{m\omega} \\ a &= \frac{m\omega}{2 \sin \omega t} \cos \omega t \end{aligned}$$

Therefore the full propagator takes the form

$$A \exp \left( \frac{i m \omega}{2 \hbar \sin \omega t} (\cos \omega t (x^2 + x'^2) - 2 x x') \right)$$

(b)

$$\begin{aligned} K &= \sqrt{\frac{m\omega}{2\pi i \hbar \sin \omega t}} \\ &= \sqrt{\frac{m\omega}{\pi \hbar}} (2i \sin \omega t)^{-1/2} \\ &= \sqrt{\frac{m\omega}{\pi \hbar}} (e^{i\omega t} - e^{-i\omega t})^{-1/2} \\ &= \sqrt{\frac{m\omega}{\pi \hbar}} e^{-i\omega t/2} (1 - e^{-2i\omega t})^{-1/2} \\ &= \sqrt{\frac{m\omega}{\pi \hbar}} e^{-i\omega t/2} \sum_{i=0}^{\infty} a_i e^{-2i\omega t} \end{aligned}$$

where  $a_n$  is the expansion coefficient of  $(1 - x)^{1/2}$ . The states in between are missing due to the zero in the wavefunction.

(c)

$$\begin{aligned}
 K &= \sqrt{\frac{m\omega}{2\pi i \hbar \sin \omega t}} \exp\left(\frac{i m \omega x^2}{\hbar \sin \omega t} (\cos \omega t - 1)\right) \\
 \int K dx &= \sqrt{\frac{m\omega}{2\pi i \hbar \sin \omega t}} \exp\left(\frac{i m \omega x^2}{\hbar \sin \omega t} (\cos \omega t - 1)\right) \\
 &= \sqrt{\frac{m\omega}{2\pi i \hbar \sin \omega t} \frac{i \pi \hbar \sin \omega t}{m\omega (\cos \omega t - 1)}} \\
 &= \sqrt{\frac{1}{(\cos \omega t - 1)}} \\
 &= \frac{1}{2i \sin(\omega t/2)} \\
 &= (e^{i\omega t/2} - e^{-i\omega t/2})^{-1} \\
 &= e^{-i\omega t/2} (1 - e^{-i\omega t})^{-1} \\
 &= \sum_{n=0}^{\infty} \exp\left(-i\omega t \left(n + \frac{1}{2}\right)\right)
 \end{aligned}$$

**3.**

(a)

Function to minimize

$$\begin{aligned}
 E &= \int d^3r \varphi^* H \varphi - \varepsilon \left( \int d^3r \varphi^* \varphi - 1 \right) \\
 &= \int d^3r (\alpha \psi_A + \beta \psi_B) \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} + \frac{e^2}{R} \right) (\alpha \psi_A + \beta \psi_B) \\
 &\quad - \varepsilon \left( \int d^3r (\alpha \psi_A + \beta \psi_B)^2 - 1 \right)
 \end{aligned}$$

Expanding derivative around the center of the wavefunctions

$$\begin{aligned}
 E &= \alpha \int d^3r (\alpha \psi_A + \beta \psi_B) \left( E_{1s} - \frac{e^2}{r_{1B}} + \frac{e^2}{R} \right) \psi_A \\
 &\quad + \beta \int d^3r (\alpha \psi_A + \beta \psi_B) \left( E_{1s} - \frac{e^2}{r_{1A}} + \frac{e^2}{R} \right) \psi_B \\
 &\quad - \varepsilon \left( \int d^3r (\alpha \psi_A + \beta \psi_B)^2 - 1 \right) \\
 &= \alpha^2 \left( E_{1s} - e^2 \int d^3r \frac{\psi_A^2}{r_{1B}} + \frac{e^2}{R} \right) + \alpha \beta \left( E_{1s} S + \frac{e^2 S}{R} - e^2 \int d^3r \frac{\psi_A \psi_B}{r_{1B}} \right) \\
 &\quad + \beta^2 \left( E_{1s} - e^2 \int d^3r \frac{\psi_B^2}{r_{1A}} + \frac{e^2}{R} \right) + \alpha \beta \left( E_{1s} S + \frac{e^2 S}{R} - e^2 \int d^3r \frac{\psi_A \psi_B}{r_{1A}} \right) \\
 &\quad - \varepsilon (\alpha^2 + 2\alpha\beta S + \beta^2 - 1)
 \end{aligned}$$

$$\text{Let } U_1 \equiv \int d^3r \frac{\psi_A^2}{r_{1B}} = \int d^3r \frac{\psi_B^2}{r_{1A}}, U_2 \equiv \int d^3r \frac{\psi_A \psi_B}{r_{1A}} = \int d^3r \frac{\psi_A \psi_B}{r_{1B}}$$

$$\begin{aligned} E &= (\alpha^2 + \beta^2) \left( E_{1s} - e^2 U_1 + \frac{e^2}{R} - \varepsilon \right) + 2\alpha\beta \left( E_{1s} S + \frac{e^2 S}{R} - e^2 U_2 - \varepsilon S \right) - \varepsilon \\ &= -(\alpha^2 + \beta^2)(e^2 U_1 + \zeta) - 2\alpha\beta(e^2 U_2 + \zeta S) - \varepsilon \end{aligned}$$

To minimize  $E$

$$\begin{aligned} 0 &= \alpha^2 + 2\alpha\beta S + \beta^2 - 1 \\ 0 &= \alpha(e^2 U_1 + \zeta) + \beta(e^2 U_2 + \zeta S) \\ 0 &= \beta(e^2 U_1 + \zeta) + \alpha(e^2 U_2 + \zeta S) \end{aligned}$$

Therefore,

$$\begin{aligned} V_{AA} &= V_{BB} = e^2 U_1 \\ V_{AB} &= V_{BA} = e^2 U_2 \end{aligned}$$

**(b)**

From normalization,

$$\alpha = \frac{1}{\sqrt{2(1+S)}}$$

Energy

$$\begin{aligned} \varepsilon &= 2\alpha^2 \left( E_{1s} - e^2 U_1 + \frac{e^2}{R} \right) + 2\alpha^2 \left( E_{1s} S + \frac{e^2 S}{R} - e^2 U_2 \right) \\ &= \frac{1}{1+S} \left( \left( E_{1s} + \frac{e^2}{R} \right) (1+S) - e^2 U_1 - e^2 U_2 \right) \\ &= E_{1s} + \frac{e^2}{R} - \frac{e^2}{1 + (1 + \rho + \rho^2/3)e^{-\rho}} \left( \frac{1}{R} (1 - (1 + \rho)e^{-2\rho}) + \frac{1}{a_0} (1 + \rho)e^{-\rho} \right) \\ f &= \frac{1 - 2\rho^2/3 + (1 + \rho)e^{-\rho}}{1 + (1 + \rho + \rho^2/3)e^{-\rho}} e^{-\rho} \end{aligned}$$

**(c)**

Effective “force”

$$\begin{aligned} F &= -\frac{d\varepsilon}{dR} \\ \frac{F a_0^2}{e^2} &= -\frac{d}{d\rho} \frac{f}{\rho} \\ &= -\frac{d}{d\rho} \frac{(3 - 2\rho^2)e^{-\rho} + (3 + 3\rho)e^{-2\rho}}{3\rho + (3\rho + 3\rho^2 + \rho^3)e^{-\rho}} \\ &= e^{-\rho} \frac{(3\rho + (3\rho + 3\rho^2 + \rho^3)e^{-\rho})((3 + 4\rho - 2\rho^2) + (3 + 6\rho)e^{-\rho})}{(3\rho + (3\rho + 3\rho^2 + \rho^3)e^{-\rho})^2} \\ &\quad + e^{-\rho} \frac{((3 - 2\rho^2) + (3 + 3\rho)e^{-\rho})(3 + (3 + 3\rho - \rho^3)e^{-\rho})}{(3\rho + (3\rho + 3\rho^2 + \rho^3)e^{-\rho})^2} \end{aligned}$$

$$\frac{F a_0^2}{e^2} e^\rho (3\rho + (3\rho + 3\rho^2 + \rho^3) e^{-\rho})^2$$

$$= 3(3 + 3\rho + 2\rho^2 - 2\rho^3) + (18 + 36\rho + 44\rho^2 - 2\rho^4) e^{-\rho} + 3(3 + 9\rho + 12\rho^2 + 6\rho^3 + \rho^4) e^{-2\rho}$$

**4.**

**(a)**

Eigenvalue equation

$$(\varepsilon - \lambda)^2 = t^2$$

$$\varepsilon - \lambda = \pm t$$

$$\lambda = \varepsilon \pm t$$

Eigenvectors  $r_1|R\rangle + r_2|R'\rangle$

$$0 = (\varepsilon - \lambda)r_1 - tr_2$$

$$r_2 = \mp r_1$$

Normalized eigenvectors

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|R\rangle \mp |R'\rangle)$$

**(b)**

$$|\Phi_H\rangle = \frac{1}{2}(|R_1\rangle + |R'_1\rangle)(|R_2\rangle + |R'_2\rangle)$$

$$= \frac{1}{2}(|RR\rangle + |RR'\rangle + |R'R\rangle + |R'R'\rangle)$$

$$= \frac{1}{\sqrt{2}}|\Phi_0\rangle + \frac{1}{2}(|\Phi_1\rangle + |\Phi_2\rangle)$$

$$E_H = 2(\varepsilon - t) + U$$

Matrix elements

$$h_1 = \begin{pmatrix} \langle \Phi_0 | h_1 | \Phi_0 \rangle & \langle \Phi_0 | h_1 | \Phi_1 \rangle & \langle \Phi_0 | h_1 | \Phi_2 \rangle \\ \langle \Phi_1 | h_1 | \Phi_0 \rangle & \langle \Phi_1 | h_1 | \Phi_1 \rangle & \langle \Phi_1 | h_1 | \Phi_2 \rangle \\ \langle \Phi_2 | h_1 | \Phi_0 \rangle & \langle \Phi_2 | h_1 | \Phi_1 \rangle & \langle \Phi_2 | h_1 | \Phi_2 \rangle \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2}(\langle R | h_1 | R \rangle + \langle R' | h_1 | R' \rangle) & \frac{1}{\sqrt{2}}\langle R' | h_1 | R \rangle & \frac{1}{\sqrt{2}}\langle R | h_1 | R' \rangle \\ \frac{1}{\sqrt{2}}\langle R | h_1 | R' \rangle & \langle R | h_1 | R \rangle & 0 \\ \frac{1}{\sqrt{2}}\langle R' | h_1 | R \rangle & 0 & \langle R' | h_1 | R' \rangle \end{pmatrix}$$

$$= \begin{pmatrix} \varepsilon & \frac{t}{\sqrt{2}} & \frac{t}{\sqrt{2}} \\ \frac{t}{\sqrt{2}} & \varepsilon & 0 \\ \frac{t}{\sqrt{2}} & 0 & \varepsilon \end{pmatrix}$$

Similarly

$$h_2 = \begin{pmatrix} \varepsilon & \frac{t}{\sqrt{2}} & \frac{t}{\sqrt{2}} \\ \frac{t}{\sqrt{2}} & \varepsilon & 0 \\ \frac{t}{\sqrt{2}} & 0 & \varepsilon \end{pmatrix}$$

$$V_{12} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & U \end{pmatrix}$$

$$H = \begin{pmatrix} 2\varepsilon & \sqrt{2}t & \sqrt{2}t \\ \sqrt{2}t & 2\varepsilon + U & 0 \\ \sqrt{2}t & 0 & 2\varepsilon + U \end{pmatrix}$$

$$\alpha = \sqrt{2}$$

(c)

$$0 = (2\varepsilon - \lambda)(2\varepsilon + U - \lambda)^2 - 4t^2(2\varepsilon + U - \lambda)$$

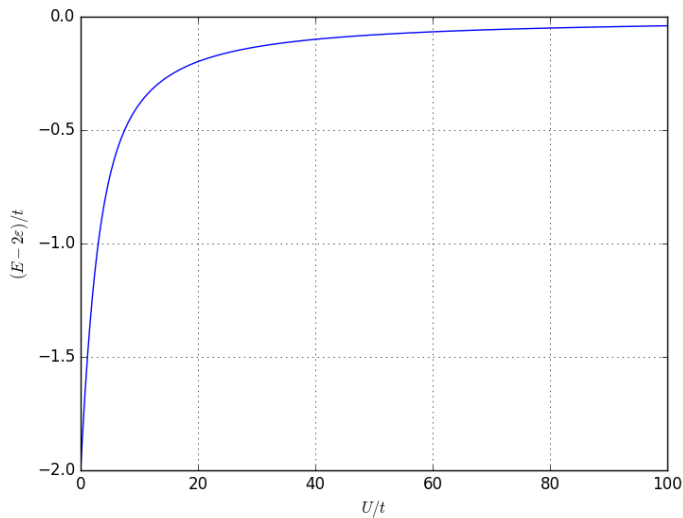
$$\lambda_1 = 2\varepsilon + U$$

$$0 = (2\varepsilon - \lambda)(2\varepsilon + U - \lambda) - 4t^2$$

$$0 = (2\varepsilon - \lambda)^2 + U(2\varepsilon - \lambda) - 4t^2$$

$$\lambda_{2,3} = 2\varepsilon + \frac{U \pm \sqrt{U^2 + 16t^2}}{2}$$

Therefore  $E_{exact} = 2\varepsilon + \frac{U - \sqrt{U^2 + 16t^2}}{2}$



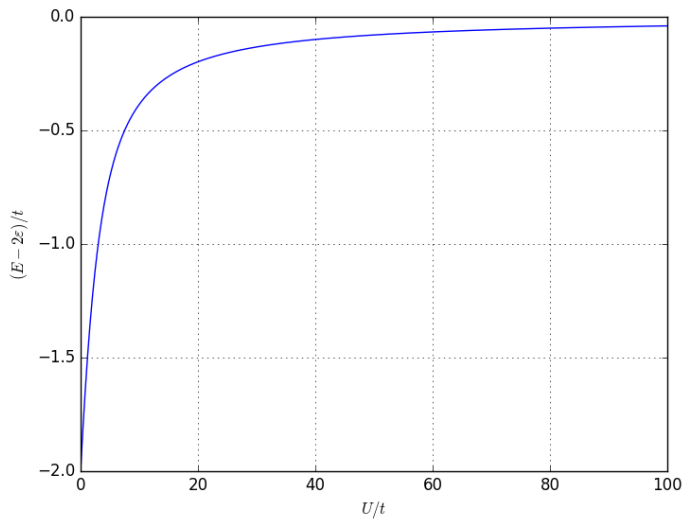
For small  $u$  this fallback to the non-interacting case, for large  $U$ , this fallback to separate atom case.

(d)

The eigenstate corresponds to  $\lambda_1$  is  $|\Phi_1\rangle - |\Phi_2\rangle$  so other eigenstates has to take the form  $\frac{1}{\sqrt{2}}|\Phi_0\rangle + \frac{f(u)}{2}(|\Phi_1\rangle + |\Phi_2\rangle)$  in order to be orthogonal to it. Substitute to  $H$

$$\begin{aligned} 0 &= \sqrt{2}t \frac{1}{\sqrt{2}} + \frac{U + \sqrt{U^2 + 16t^2}}{2} \frac{f}{2} \\ f &= - \frac{4t}{U + \sqrt{U^2 + 16t^2}} \\ &= \frac{u - \sqrt{u^2 + 16}}{4} \end{aligned}$$

The probability of finding two electron on the same proton is  $\frac{f^2}{1 + f^2}$



For small  $u$  this fallback to the non-interacting case, for large  $U$ , the atom will stay on different protons due to repulsion.