1. Gauge invariance and the Lorentz force

(a)

Schroedinger equation

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

Complex conjugate

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

(b)

Under time reversal transformation

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

(c)

Derivatives,

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

Euler-Lagrange equation

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

2.

(a)

(b)

(c)

3.

(a)

Function to minimize

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

Expanding derivative around the center of the wavefunctions

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

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

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

To minimize E

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

Therefore,

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

(b)

From normalization,

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

Energy

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

(c)

Effective "force"

$$\begin{aligned}
F =&-\frac{\mathrm{d}\varepsilon}{\mathrm{d}R}\\
\frac{Fa_0^2}{e^2} =&-\frac{\mathrm{d}}{\mathrm{d}\rho}\frac{f}{\rho}\\
=&-\frac{\mathrm{d}}{\mathrm{d}\rho}\frac{(3-2\rho^2)\mathrm{e}^{-\rho}+(3+3\rho)\mathrm{e}^{-2\rho}}{3\rho+(3\rho+3\rho^2+\rho^3)\mathrm{e}^{-\rho}}\\
=&\mathrm{e}^{-\rho}\frac{\left(3\rho+\left(3\rho+3\rho^2+\rho^3\right)\mathrm{e}^{-\rho}\right)\left(\left(3+4\rho-2\rho^2\right)+(3+6\rho)\mathrm{e}^{-\rho}\right)}{\left(3\rho+(3\rho+3\rho^2+\rho^3)\mathrm{e}^{-\rho}\right)^2}\\
&+\mathrm{e}^{-\rho}\frac{\left(\left(3-2\rho^2\right)+(3+3\rho)\mathrm{e}^{-\rho}\right)\left(3+\left(3+3\rho-\rho^3\right)\mathrm{e}^{-\rho}\right)}{\left(3\rho+(3\rho+3\rho^2+\rho^3)\mathrm{e}^{-\rho}\right)^2}
\end{aligned}$$

$$\begin{aligned}
&\frac{Fa_0^2}{e^2}\mathrm{e}^{\rho}\big(3\rho+\big(3\rho+3\rho^2+\rho^3\big)\mathrm{e}^{-\rho}\big)^2\\
=&3\big(3+3\rho+2\rho^2-2\rho^3\big)+\big(18+36\rho+44\rho^2-2\rho^4\big)\mathrm{e}^{-\rho}+3\big(3+9\rho+12\rho^2+6\rho^3+\rho^4\big)\mathrm{e}^{-2\rho}
\end{aligned}$$

4.

(a)

Eigenvalue equation

$$\begin{aligned}
(\varepsilon-\lambda)^2=&t^2\\
\varepsilon-\lambda=&\pm t\\
\lambda=&\varepsilon\pm t
\end{aligned}$$

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

$$\begin{aligned}
0=&(\varepsilon-\lambda)r_1-tr_2\\
r_2=&\mp r_1
\end{aligned}$$

Normalized eigenvectors

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

(b)

$$\begin{aligned}
|\Phi_H\rangle=&\frac{1}{2}(|R_1\rangle+|R_1'\rangle)(|R_2\rangle+|R_2'\rangle)\\
=&\frac{1}{2}(|RR\rangle+|RR'\rangle+|R'R\rangle+|R'R'\rangle)\\
=&\frac{1}{\sqrt{2}}|\Phi_0\rangle+\frac{1}{2}(|\Phi_1\rangle+|\Phi_2\rangle)\\
E_H=&2(\varepsilon-t)+U
\end{aligned}$$

Matrix elements

$$\begin{aligned}
h_1=&\begin{pmatrix}\langle\Phi_0|h_1|\Phi_0\rangle & \langle\Phi_0|h_1|\Phi_1\rangle & \langle\Phi_0|h_1|\Phi_2\rangle\\ \langle\Phi_1|h_1|\Phi_0\rangle & \langle\Phi_1|h_1|\Phi_1\rangle & \langle\Phi_1|h_1|\Phi_2\rangle\\ \langle\Phi_2|h_1|\Phi_0\rangle & \langle\Phi_2|h_1|\Phi_1\rangle & \langle\Phi_2|h_1|\Phi_2\rangle\end{pmatrix}\\
=&\begin{pmatrix}\frac{1}{2}(\langle R|h_1|R\rangle+\langle R'|h_1|R'\rangle) & \frac{1}{\sqrt{2}}\langle R'|h_1|R\rangle & \frac{1}{\sqrt{2}}\langle R|h_1|R'\rangle\\ \frac{1}{\sqrt{2}}\langle R|h_1|R'\rangle & \langle R|h_1|R\rangle & 0\\ \frac{1}{\sqrt{2}}\langle R'|h_1|R\rangle & 0 & \langle R'|h_1|R'\rangle\end{pmatrix}\\
=&\begin{pmatrix}\varepsilon & \frac{t}{\sqrt{2}} & \frac{t}{\sqrt{2}}\\ \frac{t}{\sqrt{2}} & \varepsilon & 0\\ \frac{t}{\sqrt{2}} & 0 & \varepsilon\end{pmatrix}
\end{aligned}$$

Similarly

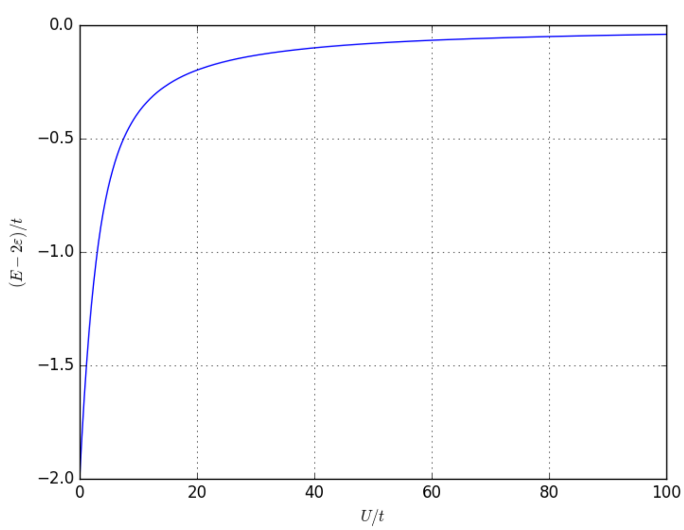
$$h_2 = \begin{pmatrix} \varepsilon & \frac{t}{\sqrt{2}} & \frac{t}{\sqrt{2}} \\ \frac{t}{\sqrt{2}} & \varepsilon & 0 \\ \frac{t}{\sqrt{2}} & 0 & \varepsilon \end{pmatrix}$$
$$V_{12} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & U \end{pmatrix}$$
$$H = \begin{pmatrix} 2\varepsilon & \sqrt{2}t & \sqrt{2}t \\ \sqrt{2}t & 2\varepsilon + U & 0 \\ \sqrt{2}t & 0 & 2\varepsilon + U \end{pmatrix}$$

$\alpha = \sqrt{2}$

(c)

$$\begin{aligned}
0 =& (2\varepsilon - \lambda)(2\varepsilon + U - \lambda)^2 - 4t^2(2\varepsilon + U - \lambda) \\
\lambda_1 =& 2\varepsilon + U \\
0 =& (2\varepsilon - \lambda)(2\varepsilon + U - \lambda) - 4t^2 \\
0 =& (2\varepsilon - \lambda)^2 + U(2\varepsilon - \lambda) - 4t^2 \\
\lambda_{2,3} =& 2\varepsilon + \frac{U \pm \sqrt{U^2 + 16t^2}}{2}
\end{aligned}$$

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



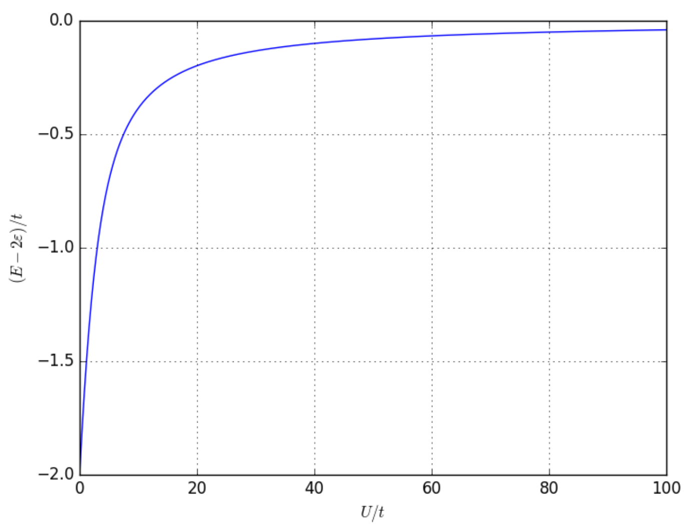
For small u this fallback to the non-interacting case, for large U, this fallback to separate atom case.

(d)

The eigenstate corresponds to λ_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 $\dfrac{f^2}{1 + f^2}$



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