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

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

2.

(a)

For each step

$$K(x_{j+1}, x_j; \varepsilon) = \sqrt{\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}}\exp\left(\frac{\mathrm{i}}{\hbar}\left(a_1\left(x_{j+1}^2 + x_j^2\right) - 2b_1x_{j+1}x_j\right)\right)$$

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

$$\begin{aligned}
&\left(\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}\right)^{n/2}\prod_{j=1}^n\int\mathrm{d}x_{j-1}\exp\left(\frac{\mathrm{i}}{\hbar}\sum_{j=1}^n\left(a_1\left(x_{j-1}^2 + x_j^2\right) - 2b_1x_{j-1}x_j\right)\right)\\
=& A_n\exp\left(\frac{\mathrm{i}}{\hbar}\left(a_n\left(x_n^2 + x_0^2\right) - 2b_nx_nx_0\right)\right)
\end{aligned}$$

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

$$\begin{aligned}
&A_{n+1}\exp\left(\frac{\mathrm{i}}{\hbar}\left(a_{n+1}\left(x_0^2 + x_{n+1}^2\right) - 2b_{n+1}x_0x_{n+1}\right)\right)\\
=& A_n\left(\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}\right)^{1/2}\int\mathrm{d}x_n\exp\left(\frac{\mathrm{i}}{\hbar}\left(a_1\left(x_{n+1}^2 + x_n^2\right) - 2b_1x_{n+1}x_n + a_n\left(x_n^2 + x_0^2\right) - 2b_nx_nx_0\right)\right)\\
=& A_n\left(\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}\right)^{1/2}\int\mathrm{d}x_n\exp\left(\frac{\mathrm{i}}{\hbar}\left((a_1 + a_n)x_n^2 - 2(b_1x_{n+1} + b_nx_0)x_n + a_1x_{n+1}^2 + a_nx_0^2\right)\right)\\
=& A_n\left(\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}\right)^{1/2}\sqrt{\frac{\mathrm{i}\pi\hbar}{a_1 + a_n}}\exp\left(\frac{\mathrm{i}}{\hbar}\left(-\frac{(b_1x_{n+1} + b_nx_0)^2}{a_1 + a_n} + a_1x_{n+1}^2 + a_nx_0^2\right)\right)\\
=& A_n\left(\frac{m}{2\pi\mathrm{i}\hbar\varepsilon}\right)^{1/2}\sqrt{\frac{\mathrm{i}\pi\hbar}{a_1 + a_n}}\exp\left(\frac{\mathrm{i}}{\hbar}\left(\left(a_1 - \frac{b_1^2}{a_1 + a_n}\right)\left(x_{n+1}^2 + x_0^2\right) - 2\frac{b_1b_n}{a_1 + a_n}x_{n+1}x_0\right)\right)
\end{aligned}$$

So $a_{n+1}=a_1-\dfrac{b_1^2}{a_1+a_n}$, $b_{n+1}=\dfrac{b_1b_n}{a_1+a_n}$, which also satisfy $a_{n+1}^2-b_{n+1}^2=a_1^2-b_1^2$. Let $\dfrac{\omega\varepsilon}{2}=\sin\dfrac{\tilde\omega\varepsilon}{2}$

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

In the small ε 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

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

(b)

(c)

3.

(a)

Function to minimize

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

Expanding derivative around the center of the wavefunctions

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

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

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

To minimize E

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

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

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

(c)

Effective "force"

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

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

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

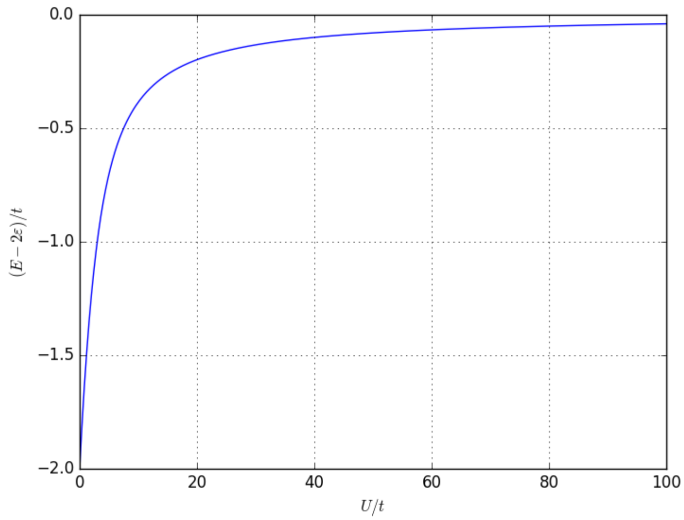
$$
\begin{aligned}
h_2 &= \begin{pmatrix} \varepsilon & \frac{t}{\sqrt{2}} & \frac{t}{\sqrt{2}} \\ \frac{t}{\sqrt{2}} & \varepsilon & 0 \\ \frac{t}{\sqrt{2}} & 0 & \varepsilon \end{pmatrix} \\
V_{12} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & U \end{pmatrix} \\
H &= \begin{pmatrix} 2\varepsilon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

$\alpha = \sqrt{2}$

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



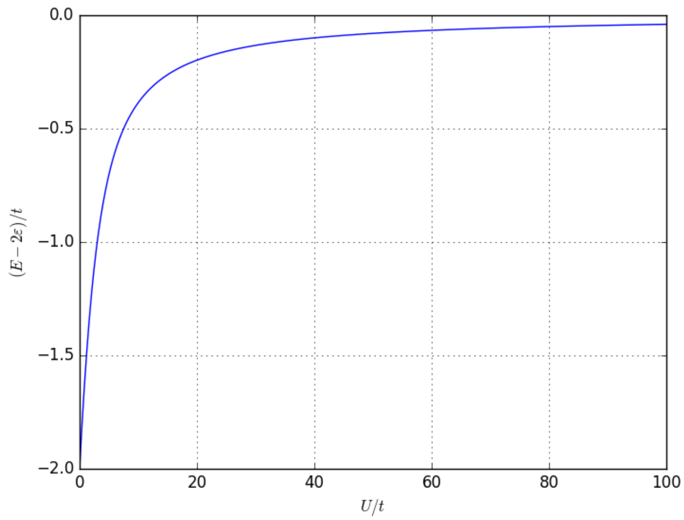
For small u this fallback to the non-interacting case, for large U, this fallback to separate atom case.

(d)

The eigenstate corresponds to λ_1 is $|\Phi_1\rangle - |\Phi_2\rangle$ so other eigenstates has to take the form $\dfrac{1}{\sqrt{2}}|\Phi_0\rangle + \frac{f(u)}{2}(|\Phi_1\rangle + |\Phi_2\rangle)$ 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.