Interaction picture for a charged particle in electromagnetic field

The gauge freedom for scalar and vector potential is given by

$$\begin{aligned}\Phi' &\to \Phi - \partial_t \chi \\ \boldsymbol{A}' &\to \boldsymbol{A} - \boldsymbol{\nabla}\chi\end{aligned} \tag{1}$$

where $\chi = \chi(\boldsymbol{r}, t)$ is some scalar function. The Schröedinger Hamiltonian for a particle in an electromagnetic field is given by

$$H = \frac{1}{2m}\left[\boldsymbol{p} + e\boldsymbol{A}\right]^2 - e\Phi + V(\boldsymbol{r}) \tag{2}$$

We can utilize the gauge freedom by moving into an interaction picture with respect to $R \equiv e^{-ie\chi/\hbar}$. We have

$$H' = RHR^\dagger + i\hbar(\partial_t R)R^\dagger \tag{3}$$

The second term is simply

$$\begin{aligned}i\hbar(\partial_t R)R^\dagger &= i\hbar\partial_t\left(e^{-ie\chi/\hbar}\right)e^{ie\chi\hbar} \\ &= e\partial_t\chi\end{aligned} \tag{4}$$

Meanwhile,

$$e^{-ie\chi/\hbar}\left[-e\Phi + V\left(\boldsymbol{r}\right)\right]e^{ie\chi/\hbar} = -e\Phi + V\left(\boldsymbol{r}\right) \tag{5}$$

so that

$$R\left[-e\Phi + V\left(\boldsymbol{r}\right)\right]R^\dagger + i\hbar\left(\partial_t R\right)R^\dagger = -e\left(\Phi - \partial_t\chi\right) + V\left(\boldsymbol{r}\right) \equiv -e\Phi' + V\left(\boldsymbol{r}\right) \tag{6}$$

By using $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$, we can write

$$\begin{aligned}\left[\boldsymbol{p} + e\boldsymbol{A}\right]^2 e^{ie\chi/\hbar}\psi &= \left[p^2 + e\boldsymbol{p}\cdot\boldsymbol{A} + e\boldsymbol{A}\cdot\boldsymbol{p} + e^2A^2\right]e^{ie\chi/\hbar}\psi \\ &= -\hbar^2\nabla^2\left(e^{ie\chi/\hbar}\psi\right) - ie\hbar\boldsymbol{\nabla}\cdot\left(\boldsymbol{A}e^{ie\chi/\hbar}\psi\right) - ie\hbar\boldsymbol{A}\cdot\boldsymbol{\nabla}\left(e^{ie\chi/\hbar}\psi\right) + e^2A^2e^{ie\chi/\hbar}\psi\end{aligned} \tag{7}$$

Now,

$$\begin{aligned}\boldsymbol{\nabla}\left(e^{ie\chi/\hbar}\psi\right) &= \psi\boldsymbol{\nabla}e^{ie\chi/\hbar} + e^{ie\chi/\hbar}\boldsymbol{\nabla}\psi \\ &= \frac{ie}{\hbar}e^{ie\chi/\hbar}\left(\boldsymbol{\nabla}\chi\right)\psi + e^{ie\chi/\hbar}\boldsymbol{\nabla}\psi\end{aligned} \tag{8}$$

which gives

$$\boldsymbol{A}\cdot\boldsymbol{\nabla}\left(e^{ie\chi/\hbar}\psi\right) = \frac{ie}{\hbar}e^{ie\chi/\hbar}\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi + e^{ie\chi/\hbar}\boldsymbol{A}\cdot\boldsymbol{\nabla}\psi \tag{9}$$

and

$$\begin{aligned}\nabla^2\left(e^{ie\chi/\hbar}\psi\right) &= \frac{ie}{\hbar}\boldsymbol{\nabla}\cdot\left(e^{ie\chi/\hbar}\psi\boldsymbol{\nabla}\chi\right) + \boldsymbol{\nabla}\cdot\left(e^{ie\chi/\hbar}\boldsymbol{\nabla}\psi\right) \\ &= \frac{ie}{\hbar}\left(\nabla^2\chi\right)e^{ie\chi/\hbar}\psi + \frac{ie}{\hbar}\left(\boldsymbol{\nabla}\chi\right)\cdot\boldsymbol{\nabla}\left(e^{ie\chi/\hbar}\psi\right) + e^{ie\chi/\hbar}\nabla^2\psi + \boldsymbol{\nabla}\psi\cdot\boldsymbol{\nabla}e^{ie\chi/\hbar} \\ &= \frac{ie}{\hbar}\left(\nabla^2\chi\right)e^{ie\chi/\hbar}\psi - \frac{e^2}{\hbar^2}\left(\boldsymbol{\nabla}\chi\right)^2e^{ie\chi/\hbar}\psi + \frac{ie}{\hbar}e^{ie\chi/\hbar}\left(\boldsymbol{\nabla}\chi\right)\cdot\boldsymbol{\nabla}\psi + e^{ie\chi/\hbar}\nabla^2\psi + \frac{ie}{\hbar}e^{ie\chi/\hbar}\left(\boldsymbol{\nabla}\chi\right)\cdot\left(\boldsymbol{\nabla}\psi\right)\end{aligned} \tag{10}$$

Furthermore,

$$\begin{aligned}\boldsymbol{\nabla}\cdot\left(\boldsymbol{A}e^{ie\chi/\hbar}\psi\right) &= (\boldsymbol{\nabla}\cdot\boldsymbol{A})e^{ie\chi/\hbar}\psi + \boldsymbol{A}\cdot\boldsymbol{\nabla}\left(e^{ie\chi/\hbar}\psi\right) \\ &= (\boldsymbol{\nabla}\cdot\boldsymbol{A})e^{ie\chi/\hbar}\psi + \frac{ie}{\hbar}e^{ie\chi/\hbar}\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi + e^{ie\chi/\hbar}\boldsymbol{A}\cdot\boldsymbol{\nabla}\psi\end{aligned} \tag{11}$$

Substituting these back into (5) and multiplying by $e^{-ie\chi/\hbar}$, we find that

$$\begin{aligned}e^{-ie\chi/\hbar}\left[\boldsymbol{p} + e\boldsymbol{A}\right]^2e^{ie\chi/\hbar}\psi = -\hbar^2&\left[\frac{ie}{\hbar}\left(\nabla^2\chi\right)\psi - \frac{e^2}{\hbar^2}\left(\boldsymbol{\nabla}\chi\right)^2\psi + \frac{2ie}{\hbar}\left(\boldsymbol{\nabla}\chi\right)\cdot\boldsymbol{\nabla}\psi + \nabla^2\psi + \frac{ie}{\hbar}\left(\boldsymbol{\nabla}\chi\right)\cdot\boldsymbol{\nabla}\psi\right] \\ &- ie\hbar\left[(\boldsymbol{\nabla}\cdot\boldsymbol{A})\psi + \frac{ie}{\hbar}\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi + \boldsymbol{A}\cdot\boldsymbol{\nabla}\psi\right] \\ &- ie\hbar\left[\frac{ie}{\hbar}\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi + \boldsymbol{A}\cdot\boldsymbol{\nabla}\psi\right] \\ &+ e^2A^2\psi\end{aligned} \tag{12}$$

Notice all the terms containing χ. We can write

$$\begin{aligned}(\boldsymbol{p}\cdot e\boldsymbol{\nabla}\chi)\,\psi &= -ie\hbar\boldsymbol{\nabla}\cdot(\psi\boldsymbol{\nabla}\chi)\\ &= -ie\hbar\left(\nabla^2\chi\right)\psi - ie\hbar\boldsymbol{\nabla}\chi\cdot\boldsymbol{\nabla}\psi\end{aligned}\tag{13}$$

and

$$(e\boldsymbol{\nabla}\chi\cdot\boldsymbol{p})\,\psi = -ie\hbar\boldsymbol{\nabla}\chi\cdot\boldsymbol{\nabla}\psi\tag{14}$$

All that is left now is to collect terms and make the appropriate substitutions to find that

$$\begin{aligned}e^{-ie\chi/\hbar}\left[\boldsymbol{p}+e\boldsymbol{A}\right]^2 e^{ie\chi/\hbar}\psi = &\left\{-\hbar^2\nabla^2\psi\right\}\\ &+\left\{\left[-ie\hbar\left(\boldsymbol{\nabla}\cdot\boldsymbol{A}\right)\psi - ie\hbar\boldsymbol{A}\cdot\boldsymbol{\nabla}\psi\right]+\left[-ie\hbar\left(\nabla^2\chi\right)\psi - ie\hbar\boldsymbol{\nabla}\chi\cdot\boldsymbol{\nabla}\psi\right]\right\}\\ &+\left\{\left[-ie\hbar\boldsymbol{A}\cdot\boldsymbol{\nabla}\psi\right]+\left[-ie\hbar\boldsymbol{\nabla}\chi\cdot\boldsymbol{\nabla}\psi\right]\right\}\\ &+\left\{\left[e^2A^2\psi\right]+\left[e^2\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi\right]+\left[e^2\left(\boldsymbol{A}\cdot\boldsymbol{\nabla}\chi\right)\psi\right]+\left[e^2\left(\boldsymbol{\nabla}\chi\right)^2\psi\right]\right\}\\ \equiv &\ p^2\psi+\left\{\boldsymbol{p}\cdot\left(\boldsymbol{eA}\psi\right)+\boldsymbol{p}\cdot\left(\psi e\boldsymbol{\nabla}\chi\right)\right\}+\left\{e\left(\boldsymbol{A}\cdot\boldsymbol{p}\right)\psi+\left(e\boldsymbol{\nabla}\chi\cdot\boldsymbol{p}\right)\psi\right\}+\left\{e\left(\boldsymbol{A}+\boldsymbol{\nabla}\chi\right)\right\}^2\psi\\ = &\ p^2\psi+\left\{\boldsymbol{p}\cdot e\left(\boldsymbol{A}+\boldsymbol{\nabla}\chi\right)\right\}\psi+\left\{e\left(\boldsymbol{A}+\boldsymbol{\nabla}\chi\right)\cdot\boldsymbol{p}\right\}\psi+\left\{e\left(\boldsymbol{A}+\boldsymbol{\nabla}\chi\right)\right\}^2\psi\\ \equiv &\left[\boldsymbol{p}+e\boldsymbol{A}'\right]^2\psi\\ R\left[\boldsymbol{p}+e\boldsymbol{A}\right]^2R^\dagger \equiv &\left[\boldsymbol{p}+e\boldsymbol{A}'\right]^2\end{aligned}\tag{15}$$

Putting this result and (6) into (3), we finally obtain

$$H' = \frac{1}{2m}\left[\boldsymbol{p}+e\boldsymbol{A}'\right]^2 - e\Phi' + V\left(\boldsymbol{r}\right)\tag{16}$$

Time-dependent perturbation theory

We found that

$$\dot{C}_l(t) = -\frac{i}{\hbar}\sum_k C_k(t)\hat{H}^{(1)}_{lk}e^{i\omega_{lk}t}\tag{1}$$

where $\hat{H}^{(1)}_{lk} = \langle l|\hat{H}^{(1)}|k\rangle$. With

$$C_l(t) = C_l^{(0)}(t)+\lambda C_l^{(1)}(t)+\lambda^2C_l^{(2)}(t)+\dots\tag{2}$$

and the understanding that $\hat{H}^(1)$ comes with its own λ, we can rewrite (1) as

$$\dot{C}_l^{(0)}+\lambda\dot{C}_l^{(1)}+\lambda^2\dot{C}_l^{(2)}+\dots = -\frac{i}{\hbar}\sum_k\left[\lambda C_k^{(0)}+\lambda^2C_k^{(1)}+\dots\right]\hat{H}^{(1)}_{lk}e^{i\omega_{lk}t}\tag{3}$$

Matching the terms of the same power of λ, we find that

$$\begin{aligned}\lambda^0:&\qquad \dot{C}_l^{(0)} = 0\\ \lambda^1:&\qquad \dot{C}_l^{(1)} = -\frac{i}{\hbar}\sum_k C_k^{(0)}\hat{H}^{(1)}_{lk}e^{i\omega_{lk}t}\\ \lambda^2:&\qquad \dot{C}_l^{(2)} = -\frac{i}{\hbar}\sum_k C_k^{(1)}\hat{H}^{(1)}_{lk}e^{i\omega_{lk}t}\\ &\qquad\vdots\end{aligned}\tag{4}$$

In general,

$$\lambda^n:\qquad \dot{C}_l^{(n)} = -\frac{i}{\hbar}\sum_k C_k^{(n-1)}\hat{H}^{(1)}_{lk}e^{i\omega_{lk}t}\tag{5}$$

In perturbation theory, we assume the driving field is so weak that the atomic populations change very little. If $C_i(0)=1$ and $C_{f\neq i}(0)=0$, then to a good approximation $C_i(t)\approx 1$ and $|C_{f\neq i}(t)\ll 1|$. The equation for λ^1 with $l\to f$ can then be written as

$$\begin{aligned}\dot{C}_f^{(1)} &\approx -\frac{i}{\hbar}C_i^{(0)}\hat{H}^{(1)}_{fi}e^{i\omega_{fi}t}\\ C_f^{(1)}(t) &\approx -\frac{i}{\hbar}\int_0^t C_i^{(0)}(t')\hat{H}^{(1)}_{fi}(t')e^{i\omega_{fi}t'}dt'\end{aligned}\tag{6}$$

Plugging this with $f \to k$ into the equation for λ^2 with $l \to f$, we obtain

$$\begin{aligned}
\dot{C}_f^{(2)} &= -\frac{i}{\hbar}\sum_k C_k^{(1)}\hat{H}_{fk}^{(1)}e^{i\omega_{fk}t} \\
C_f^{(2)}(t) &= -\frac{i}{\hbar}\sum_k \int_0^t C_k^{(1)}(t')\hat{H}_{fk}^{(1)}(t')e^{i\omega_{fk}t'}dt' \\
&\approx -\frac{i}{\hbar}\sum_k \int_0^t \left(-\frac{i}{\hbar}\int_0^{t'} C_i^{(0)}(t'')\hat{H}_{ki}^{(1)}(t'')e^{i\omega_{ki}t''}dt''\right)\hat{H}_{fk}^{(1)}(t')e^{i\omega_{fk}t'}dt' \\
&= \left(-\frac{i}{\hbar}\right)^2 \sum_k \int_0^t dt' \int_0^{t'} dt'' \left[\hat{H}_{fk}^{(1)}(t')e^{i\omega_{fk}t'}\right]\left[\hat{H}_{ki}^{(1)}(t'')e^{i\omega_{ki}t''}\right]C_i^{(0)}(t'')
\end{aligned} \tag{7}$$