Title: Phase Mixing in Time-Dependent Quantum Mechanics
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At the end of the last post, we found that for time-dependent Hermitian Hamiltonian systems with the wavefunction written in terms of the instantaneous energy eigenstates, we find that:

$$\frac{\partial c_m\left(t\right)}{\partial t} = -\sum_{n=-\infty}^{\infty} c_n\left(t\right) \left\langle \psi_m\left(\mathbf{r},t\right)\right| \left(\frac{\partial}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle\right) e^{-\frac{i\int_{t_0}^{t} \mathrm{d}t_1\,\left(E_n\left(t_1\right)-E_m\left(t_1\right)\right)}{\hbar}} \tag{1}$$

where $c_n\left(t\right)$ are the probability amplitudes of the $\left|\psi_n\left(\mathbf{r},t\right)\right\rangle$ time-dependent energy eigenstates with $E_n\left(t\right)$ time-dependent energy eigenvalues, which are defined by the linear relation:

$$\begin{aligned}
\hat{H}\left(t\right)\left|\psi_n\left(\mathbf{r},t\right)\right\rangle &= E_n\left(t\right)\left|\psi_n\left(\mathbf{r},t\right)\right\rangle \\
\implies \frac{\partial \hat{H}\left(t\right)}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle + \hat{H}\left(t\right)\frac{\partial\left|\psi_n\left(\mathbf{r},t\right)\right\rangle}{\partial t} &= \frac{\partial E_n\left(t\right)}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle + E_n\left(t\right)\frac{\partial\left|\psi_n\left(\mathbf{r},t\right)\right\rangle}{\partial t} \\
\implies \left\langle\psi_m\left(\mathbf{r},t\right)\right|\frac{\partial \hat{H}\left(t\right)}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle &= \left\langle\psi_m\left(\mathbf{r},t\right)\right|\left(E_n\left(t\right)-\hat{H}\left(t\right)\right)\frac{\partial\left|\psi_n\left(\mathbf{r},t\right)\right\rangle}{\partial t} \\
\implies \left\langle\psi_m\left(\mathbf{r},t\right)\right|\frac{\partial}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle &= \frac{\left\langle\psi_m\left(\mathbf{r},t\right)\right|\frac{\partial\hat{H}(t)}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle}{E_n\left(t\right)-E_m\left(t\right)},\ \text{where}\, n\neq m
\end{aligned} \tag{2}$$

This formula assumes no degeneracy in the eigenstates. Of course, there also exists a sister equation known as the Hellmann-Feynman theorem that involves taking the inner product of the time derivative of the same eigenvalue-eigenstate relation using the nth eigenstate rather than the mth one, thus getting the diagonal elements of $\frac{\partial\hat{H}(t)}{\partial t}$.

$$\frac{\partial E_n\left(t\right)}{\partial t} = \left\langle\psi_n\left(\mathbf{r},t\right)\right|\frac{\partial\hat{H}\left(t\right)}{\partial t}\left|\psi_n\left(\mathbf{r},t\right)\right\rangle \tag{3}$$

One may be curious as to why Equation 2 exists at all. After all, don't all the off-diagonal matrix elements of $\hat{H}\left(t\right)$ vanish in the instantaneous energy eigenbasis? This conceptual criticism is resolved by thinking about what the partial time derivative really means in this context. First off, the time derivative indicates only the rate of change in the elements of the Hamiltonian with respect to the specific set of basis vectors at the instant that the derivative is evaluated. Since the eigenbasis is changing, this means that the Hamiltonian only stays diagonal as long as the eigenbasis is updated at the next time step. Furthermore, the partial time derivative evaluates the change in the Hamiltonian at a "frozen" picture of the eigenbasis. Thus, the Hamiltonian's time derivative's expectation value of the nth and mth states (the off-diagonal elements) are non-zero, and are a function of the expectation value of the time derivative of the eigenbasis at the given instant. Furthermore, summing Equation 1 over m and inserting Equation 2 and 3, we get:

$$\begin{aligned}\frac{\partial c_m(t)}{\partial t}+c_m(t)\langle\psi_m(\mathbf{r},t)|\frac{\partial}{\partial t}|\psi_m(\mathbf{r},t)\rangle+\sum_{n\neq m}^{\infty}c_n(t)\frac{\langle\psi_m(\mathbf{r},t)|\frac{\partial\hat{H}(t)}{\partial t}|\psi_n(\mathbf{r},t)\rangle}{E_n(t)-E_m(t)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}&=0\\ \frac{\partial c_m(t)}{\partial t}-ic_m(t)\mathcal{A}_m(t)+\sum_{n\neq m}^{\infty}c_n(t)\frac{\langle\psi_m(\mathbf{r},t)|\frac{\partial\hat{H}(t)}{\partial t}|\psi_n(\mathbf{r},t)\rangle}{E_n(t)-E_m(t)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}&=0\end{aligned}\tag{4}$$

where $\mathcal{A}_m$ is a purely real valued function, defined as:

$$\mathcal{A}_m=i\langle\psi_m(\mathbf{r},t)|\frac{\partial}{\partial t}|\psi_m(\mathbf{r},t)\rangle$$

where $\langle\psi_n(\mathbf{r},t)|\frac{\partial}{\partial t}|\psi_n(\mathbf{r},t)\rangle$ and is found to be purely imaginary according to the following logic:

$$\begin{aligned}\langle\psi_n(\mathbf{r},t)|\psi_n(\mathbf{r},t)\rangle&=1\\ \implies\frac{\partial}{\partial t}\langle\psi_n(\mathbf{r},t)|\psi_n(\mathbf{r},t)\rangle&=0\\ \implies\left\langle\frac{\partial\psi_n(\mathbf{r},t)}{\partial t}\middle|\psi_n(\mathbf{r},t)\right\rangle+\left\langle\psi_n(\mathbf{r},t)\middle|\frac{\partial\psi_n(\mathbf{r},t)}{\partial t}\right\rangle&=0\\ \implies\left(\left\langle\psi_n(\mathbf{r},t)\middle|\frac{\partial\psi_n(\mathbf{r},t)}{\partial t}\right\rangle\right)^*+\left\langle\psi_n(\mathbf{r},t)\middle|\frac{\partial\psi_n(\mathbf{r},t)}{\partial t}\right\rangle&=0\end{aligned}\tag{5}$$

and the definition of the purely imaginary complex number (where the sum of the number and its complex conjugate is equal to 0) arises. Given the second line in Equation 4, we can make a further Equation for the real part:

$$\mathrm{Re}\left(\frac{1}{c_m(t)}\frac{\partial c_m(t)}{\partial t}\right)+\mathrm{Re}\left(\sum_{n\neq m}^{\infty}\frac{c_n(t)}{c_m(t)}\frac{\langle\psi_m(\mathbf{r},t)|\frac{\partial\hat{H}(t)}{\partial t}|\psi_n(\mathbf{r},t)\rangle}{E_n(t)-E_m(t)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}\right)=0\tag{6}$$

An important is that $\frac{\partial\hat{H}}{\partial t}$ is also Hermitian, as indicated by the limit definition of the derivative (since $\hat{H}$ is Hermitian for all time, where time is a real parameter):

$$\frac{\partial\hat{H}(t)}{\partial t}=\lim_{\delta t\to0}\frac{\hat{H}(t+\delta t)-\hat{H}(t)}{\delta t}=\lim_{\delta t\to0}\frac{\hat{H}^\dagger(t+\delta t)-\hat{H}^\dagger(t)}{\delta t}$$

This Hermitian property ($\frac{\partial\hat{H}}{\partial t}=\left(\frac{\partial\hat{H}}{\partial t}\right)^\dagger$) implies that this Hamiltonian time derivative has its own *distinct* eigenvalue equation, which will be written here as:

$$\frac{\partial\hat{H}(t)}{\partial t}|\phi_q(\mathbf{r},t)\rangle=\lambda_q(t)|\phi_q(\mathbf{r},t)\rangle\tag{7}$$

and of course, from linear algebra, we know that for orthonormal eigenbasis, we get:

$$\mathbb{I}=\sum_{q}^{\infty}|\phi_q(\mathbf{r},t)\rangle\langle\phi_q(\mathbf{r},t)|=\sum_{n}^{\infty}|\psi_n(\mathbf{r},t)\rangle\langle\psi_n(\mathbf{r},t)|\tag{8}$$

which holds for all $\mathbf{r}$ and t granted that both eigenvectors in each term are evaluated at the same time and position. This step allows us to rewrite the real part equation as follows:

$$\operatorname{Re}\left(\frac{1}{c_m(t)}\frac{\partial c_m(t)}{\partial t}\right)+\operatorname{Re}\left(\sum_{n\neq m}^{\infty}\sum_{q}^{\infty}\frac{c_n(t)\,d_{nmq}(t)\,\lambda_q(t)}{c_m(t)\left(E_n(t)-E_m(t)\right)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}\right)=0 \tag{9}$$

where:

$$d_{nmq}(t)=\langle\psi_m(\mathbf{r},t)|\phi_q(\mathbf{r},t)\rangle\,\langle\phi_q(\mathbf{r},t)|\psi_n(\mathbf{r},t)\rangle$$

where we recall that the inner product represents a quantity that is independent of position - in the wavefunction interpretation of quantum mechanics, the inner product corresponds to the wavefunctions integrated over all space. Thus, we have it - a non-linear, infinite term ODE in terms of the probability amplitudes, eigenvalues, and other constants that yields information about the mth probability amplitude. There is an additional relation using the imaginary part:

$$\operatorname{Im}\left(\frac{1}{c_m(t)}\frac{\partial c_m(t)}{\partial t}\right)+\operatorname{Im}\left(\sum_{n\neq m}^{\infty}\sum_{q}^{\infty}\frac{c_n(t)\,d_{nmq}(t)\,\lambda_q(t)}{c_m(t)\left(E_n(t)-E_m(t)\right)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}\right)=\mathcal{A}_m(t) \tag{10}$$

The Equation 9 and Equation 10 hold for all t, but assume no degeneracy in the eigenstates and that the orthogonal eigenstates form an infinite dimensional basis. If there is degeneracy in the eigenstates, then for the calculation for Equation 2 is different as the states need not be orthogonal. The calculation goes as follows for degenerate energy eigenstates p, ℓ:

$$\begin{aligned}\frac{\langle\psi_\ell(\mathbf{r},t)|\,\frac{\partial\hat{H}(t)}{\partial t}\,|\psi_p(\mathbf{r},t)\rangle}{\langle\psi_\ell(\mathbf{r},t)|\psi_p(\mathbf{r},t)\rangle}&=\frac{\partial E_p(t)}{\partial t}\\ \implies\sum_{q}^{\infty}\frac{\langle\psi_\ell(\mathbf{r},t)|\phi_q(\mathbf{r},t)\rangle\,\langle\phi_q(\mathbf{r},t)|\psi_p(\mathbf{r},t)\rangle}{\langle\psi_\ell(\mathbf{r},t)|\psi_p(\mathbf{r},t)\rangle}\lambda_q(t)=\sum_{q}^{\infty}\frac{d_{p\ell q}\lambda_q(t)}{\langle\psi_\ell(\mathbf{r},t)|\psi_p(\mathbf{r},t)\rangle}&=\frac{\partial E_p(t)}{\partial t}\end{aligned} \tag{11}$$

Notice that when the degenerates states are also orthogonal, $\frac{\partial E_p(t)}{\partial t}$ is the eigenvalue of $\frac{\partial\hat{H}(t)}{\partial t}$ in the energy eigenbasis. In this case, for degenerate, orthogonal eigenvectors $|\psi_p(\mathbf{r},t)\rangle\,,|\psi_\ell(\mathbf{r},t)\rangle$ - we find that $\frac{\partial\hat{H}(t)}{\partial t}$ is diagonal in the degenerate subspace of the energy eigenbasis. For the presence of S general, non-orthogonal eigenstates that are degenerate with the mth state, the analog Equations to 9 and 10 are:

$$\begin{aligned}\frac{\partial c_m(t)}{\partial t}&+\sum_{s=\{S\}}c_s(t)\,\langle\psi_m(\mathbf{r},t)|\,\frac{\partial}{\partial t}\,|\psi_s(\mathbf{r},t)\rangle\\&+\sum_{n\neq\{S\}}^{\infty}c_n(t)\,\frac{\langle\psi_m(\mathbf{r},t)|\,\frac{\partial\hat{H}(t)}{\partial t}\,|\psi_n(\mathbf{r},t)\rangle}{E_n(t)-E_m(t)}e^{-\frac{i\int_{t_0}^{t}\mathrm{d}t_1\,(E_n(t_1)-E_m(t_1))}{\hbar}}=0\end{aligned} \tag{12}$$

To simplify the mathematics, we can use the Gram-Schmidt process to form an orthonormal subspace basis from the degenerate, non-orthogonal basis of eigenvectors. Then, the orthogonal basis can be written as in Equation 4, with the newly orthogonal degenerate subspace basis states still having the same eigenvalues. In the next post, I will explore the Gram-Schmidt process for solving problems in quantum systems, including the importance of basis consistent basis writing and the impact of changing basis in some classic problems. This is a bit of a detour from the very general formalism specified above, but I get the feeling that I will return to the general formalism stronger and more knowledgeable. Also, it is completely possible that I will find that the above formulas are in error in some way when I start trying to solve real applications with them. This concludes this blog post.