Monday, 19 September 2022

Solutions to exercises on Response Theory

Problem 1

$$i\hbar \frac{\partial}{\partial t} \psi(t) = i\hbar \frac{\partial}{\partial t} \left(\hat{U}(t)\, \psi(0) \right)$$

$$= i\hbar \frac{\partial}{\partial t} \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(-i \frac{\hat{H} t}{\hbar} \right)^n \right) \psi(0)$$

$$= i\hbar \left(\sum_{n=1}^{\infty} \frac{1}{(n-1)!} \left(-i \frac{\hat{H}}{\hbar} \right)^n t^{n-1} \right) \psi(0)$$

$$= i\hbar \left(-i \frac{\hat{H}}{\hbar} \right) \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(-i \frac{\hat{H} t}{\hbar} \right)^n \right) \psi(0)$$

$$= \hat{H}\, e^{-i \frac{\hat{H} t}{\hbar}} \psi(0) = \hat{H}\, \psi(t) \quad \checkmark$$

With a time-dependent Hamiltonian a propagator is not readily formed in this manner. We can, however, make use of this result even in the time-dependent case by discretising the time axis and approximate the external electric field by a piecewise constant field. With small time steps the error will be correspondingly small and for all practical purposes we can create a propagator also in the TD case.

Infinitesimal Time Propagation

With a time step Δt that is small, we can consider the external field to be constant between t_0 and $t_0 + \Delta t$ and thereby get

$$\psi(t_0 + \Delta t) = \hat{U}(t_0, t_0 + \Delta t)\psi(t_0)$$

where the time-evolution propagator equals

$$\hat{U}(t_0, t_0 + \Delta t) = e^{-i\hat{H}(t_0)\Delta t/\hbar}$$

Time Propagation

Repeated application of $\hat{U}$ enables us to determine the wave function in the region $t > 0$, and, given the time-dependent wave function, the dipole moment is obtained as the expectation value of the electric dipole operator according to

$$\mu(t) = \langle \psi(t) | \hat{\mu} | \psi(t) \rangle$$

Problem 2

$$\hat{P}(t)|0\rangle = \sum_{n>0} P_n |n\rangle, \tag{5.83}$$

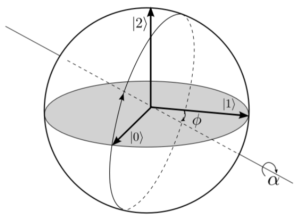
$$\hat{P}(t)^2|0\rangle = |0\rangle \sum_{n>0} |P_n|^2, \tag{5.84}$$

and from induction it is clear that a closed-form expression for the action of the exponential operator on the ground state will be

$$e^{-i\hat{P}(t)}|0\rangle = |0\rangle \cos\alpha - i \sum_{n>0} P_n |n\rangle \frac{\sin\alpha}{\alpha}, \tag{5.85}$$

$$\alpha = \sqrt{\sum_{n>0} |P_n|^2}. \tag{5.86}$$

Parametrization by rotations



$$|\bar{\psi}(t)\rangle = e^{-i\hat{P}(t)}|0\rangle; \qquad \hat{P}(t) = \sum_{n>0}\left[P_n(t)|n\rangle\langle 0| + P_n^*(t)|0\rangle\langle n|\right]$$

$$e^{-i\hat{P}(t)}|0\rangle = |0\rangle\cos\alpha - i\sum_{n>0} P_n|n\rangle\frac{\sin\alpha}{\alpha}; \qquad \alpha = \sqrt{\sum_{n>0}|P_n|^2}.$$

The key point here are that the parameterisation is without constraints; that it is complete in the sense that it can take the reference state to any point on the sphere; and that it is non-redundant, the Hermitian generator of rotations, P, is limited to include only excited-to-ground state transfer operators together with the associated amplitudes. You see in the figure a line in the complementary space of the reference state about which you rotate the reference state vector an angle alpha, which is the geometrical interpretation of the action of the transformation. One should note that it is a parameterisation for the phase isolated wave function but the wave function itself as that would require and overall phase function in addition.

Problem 3

$$
\begin{aligned}
\langle\hat{\Omega}\rangle^{(1)} &= \langle\psi^{(0)}|\hat{\Omega}|\psi^{(1)}\rangle + \langle\psi^{(1)}|\hat{\Omega}|\psi^{(0)}\rangle \\
&= -\langle 0|e^{iE_0t/\hbar}\hat{\Omega}\sum_n \frac{1}{\hbar}\sum_{\omega_1}\frac{\langle n|\hat{V}_\beta^{\omega_1}|0\rangle F_\beta^{\omega_1}}{\omega_{n0}-\omega_1-i\epsilon}\, e^{i(\omega_{n0}-\omega_1)t}e^{\epsilon t}e^{-iE_nt/\hbar}|n\rangle \\
&\quad -\sum_n \frac{1}{\hbar}\sum_{\omega_1}\frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle[F_\beta^{\omega_1}]^*}{\omega_{n0}-\omega_1+i\epsilon}\, e^{-i(\omega_{n0}-\omega_1)t}e^{\epsilon t}e^{iE_nt/\hbar}\langle n|\hat{\Omega}e^{-iE_0t/\hbar}|0\rangle \\
&= -\sum_{\omega_1}\frac{1}{\hbar}\sum_n \frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^{\omega_1}|0\rangle}{\omega_{n0}-\omega_1-i\epsilon}\, F_\beta^{\omega_1}e^{-i\omega_1 t}e^{\epsilon t} \\
&\quad -\sum_{\omega_1}\frac{1}{\hbar}\sum_n \frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}-\omega_1+i\epsilon}\, [F_\beta^{\omega_1}]^*e^{i\omega_1 t}e^{\epsilon t} \\
&= -\sum_{\omega_1}\frac{1}{\hbar}\sum_n \left[\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^{\omega_1}|0\rangle}{\omega_{n0}-\omega_1-i\epsilon} + \frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}+\omega_1+i\epsilon}\right] F_\beta^{\omega_1}e^{-i\omega_1 t}e^{\epsilon t}.
\end{aligned}
\tag{5.167}
$$

In the last step, we have made use of the fact that $[F^{\omega_1}]^* = F^{-\omega_1}$ and that ω_1 runs over both positive and negative frequencies. By a direct comparison to property-defining expansions such as that in Eq. (5.60), or a general expansion as in Eq. (5.150), we can identify the quantum-mechanical formulas for second-order properties, or linear response functions. The sum-over-states expression for the linear response function is

$$
\langle\langle\hat{\Omega};\hat{V}_\beta^{\omega}\rangle\rangle = -\frac{1}{\hbar}\sum_n\left[\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^{\omega}|0\rangle}{\omega_{n0}-\omega-i\epsilon} + \frac{\langle 0|\hat{V}_\beta^{\omega}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}+\omega+i\epsilon}\right], \tag{5.168}
$$

and that of a component of the electric-dipole polarizability tensor $\alpha_{\alpha\beta}(-\omega;\omega)$ is obtained by the substitutions $\hat{\Omega} = \hat{\mu}_\alpha$ and $\hat{V}_\beta^{\omega} = -\hat{\mu}_\beta$. It is clear that this formula can be used directly for

The key point here is the logic that we have expressions that express an observable in the presence of an external field and which DEFINES molecular properties as the expansion coefficients. Once we have written our derived formula for an exception value on EXACTLY that form we can IDENTIFY formulas for the molecular properties. This exercise does this step that allows for the identification of the expression for the polarisability.

Problem 4

Evaluate the Hessian

$$
\begin{aligned}
\left.\frac{\partial^2 E}{\partial P_n \partial P_m^*}\right|_{\mathbf{P}=0} &= -\frac{1}{2}(\langle 0|[|n\rangle\langle 0|,[|0\rangle\langle m|,\hat{H}]]|0\rangle \\
&\quad +\langle 0|[|0\rangle\langle m|,[|n\rangle\langle 0|,\hat{H}]]|0\rangle) \\
&= (E_n - E_0)\ \delta_{nm}, \\
\left.\frac{\partial^2 E}{\partial P_n^* \partial P_m^*}\right|_{\mathbf{P}=0} &= -\frac{1}{2}(\langle 0|[|0\rangle\langle n|,[|0\rangle\langle m|,\hat{H}]]|0\rangle \\
&\quad +\langle 0|[|0\rangle\langle m|,[|0\rangle\langle n|,\hat{H}]]|0\rangle) \\
&= 0.
\end{aligned}
$$

We then get

$$
\left(E^{[2]} - \hbar\omega S^{[2]}\right)^{-1} = \frac{1}{\hbar}\begin{pmatrix} \frac{1}{\omega_{n0}-\omega} & 0 \\ 0 & \frac{1}{\omega_{n0}+\omega} \end{pmatrix}
$$

For the property of interest, $\hat{\Omega} = \hat{\mu}$, we get

$$
\left[\Omega^{[1]}\right]^\dagger = \begin{pmatrix} \langle n\,|\,\hat{\mu}\,|\,0\rangle \\ -\langle 0\,|\,\hat{\mu}\,|\,n\rangle \end{pmatrix}^\dagger = \left(\langle 0\,|\,\hat{\mu}\,|\,n\rangle; -\langle n\,|\,\hat{\mu}\,|\,0\rangle\right)
$$

For the perturbation, $\hat{V}^\omega = -\hat{\mu}$, we get

$$
V^{[1]} = \begin{pmatrix} \langle n\,|-\hat{\mu}\,|\,0\rangle \\ -\langle 0\,|-\hat{\mu}\,|\,n\rangle \end{pmatrix} = \begin{pmatrix} -\langle n\,|\,\hat{\mu}\,|\,0\rangle \\ \langle 0\,|\,\hat{\mu}\,|\,n\rangle \end{pmatrix}
$$

Matrix multiplication with a diagonal matrix transforms into the desired sum-over-states expression for the polarizability.

A very convenient result of the use of the BCH expansion in response theory is that one can focus on a few of the commutators as mentioned in problem (a).

An interesting property of the Hessian is that it shows that this local analysis around the point in wave function space associated with the reference state provides you with the energies associated with all excited states that are far away on the sphere (compare with the figure of the sphere again).

Problem 5

This is shown by realising that the inverse of the diagonal matrix is equal to the same matrix after taking the inverse of the diagonal elements. Thereafter will the matrix multiplication become a sum-over-states expression.

The two terms in the sum over states expression are “hidden” in the matrix equation in terms of the block structure.

The key point is that the matrix form of the polarisability that is here presented is identical in form to the expression for the linear response function in the TDDFT approximation. Matrix elements will just be between ground and single-electron excited determinants instead of the true ground and all the excited states of the system. So the dimension of the vectors and matrices in the TDDFT approximation is *2 x nocc x nvirt* where the factor of two comes from the block structure.

In the Tamm–Dancoff approximation (TDA) of TDDFT the B-block is set to zero. The corresponding approximation in TDHF leads to the CIS approach.