

Exercise Session on Response Theory

1. Consider a system described by a time-independent Hamiltonian $\hat{H}$, which, at time $t = 0$, is found in state $\psi(0)$. Show that the wave function of the system at time $t > 0$ is given by

$$\psi(t) = \hat{U}(t)\psi(0)$$

with

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}.$$

Use this result to prove that the Schrödinger equation is norm conserving.

Note: This general result in quantum mechanics is of interest to us due to the form similarity with our parametrization of the phase isolated wave function.

2. Consider a system described by a time-dependent Hamiltonian $\hat{H}(t)$, which begins its journey in reference state $|0\rangle$. A time propagator cannot readily be formed in this case. We instead choose to parameterize the phase-isolated wave function with an explicitly unitary operator that in form is similar to the time propagator in the time-independent case.

(a) With

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

show

$$|\bar{\psi}(t)\rangle = |0\rangle \cos \alpha - i \sum_{n>0} P_n |n\rangle \frac{\sin \alpha}{\alpha}; \quad \alpha = \sqrt{\sum_{n>0} |P_n|^2}.$$

Do so by looking at the first three terms in the Taylor expansion of the operator and note a pattern.

(b) Show by explicit calculation and using the final result that

$$\langle \bar{\psi}(t) | \bar{\psi}(t) \rangle = 1$$

Note: Our parametrization based on rotations is thus unconstrained which stands in contrast to the more commonly adopted parameterizations based on projections.

Hints:

- The function of an operator is defined by the Taylor series of the function.
- $e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \dots$
- $\cos x = 1 - \frac{1}{2}x^2 + \dots$
- $\sin x = x - \frac{1}{6}x^3 + \dots$

3. The polarizability is a molecular property *defined* from the expansion of the dipole moment according to

$$\mu(t) = \mu^0 + \sum_{\omega} \alpha(\omega) F^{\omega} e^{-i\omega t} + \dots$$

Given the result

$$|\bar{\psi}^{(1)}\rangle = -i \sum_{n>0} P_n^{(1)} |n\rangle; \quad P_n^{(1)}(t) = \frac{1}{i\hbar} \sum_{\omega} \frac{\langle n | \hat{V}^{\omega} | 0 \rangle F^{\omega} e^{-i\omega t}}{\omega_{n0} - \omega}$$

form the first-order correction to an expectation value of the electric dipole moment operator, $\hat{\Omega} = \hat{\mu}$, in the electric-dipole approximation, $\hat{V}^{\omega} = -\hat{\mu}$, and *identify* the well-known sum-over-states expression for the polarizability

$$\alpha(\omega) = \frac{1}{\hbar} \sum_{n>0} \left[\frac{\langle 0 | \hat{\mu} | n \rangle \langle n | \hat{\mu} | 0 \rangle}{\omega_{n0} - \omega} + \frac{\langle 0 | \hat{\mu} | n \rangle \langle n | \hat{\mu} | 0 \rangle}{\omega_{n0} + \omega} \right].$$

Note: Such a sum-over-states expression relates a molecular property to other properties, in this case ground-to-excited state excitation energies and transition moments. This is very useful not only for property calculations but also interpretations and formations of molecular design strategies.

4. The electronic Hessian, or second-order derivative of the energy, has the block structure

$$E^{[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix}$$

where the elements of the block matrices equal

$$A_{nm} = \left. \frac{\partial^2 E}{\partial P_n \partial P_m^*} \right|_{\mathbf{P}=0}; \quad B_{nm} = \left. \frac{\partial^2 E}{\partial P_n \partial P_m} \right|_{\mathbf{P}=0}$$

We have the BCH expansion

$$e^{i\hat{P}(t)}\hat{\Omega}e^{-i\hat{P}(t)} = \hat{\Omega} + i[\hat{P}, \hat{\Omega}] - \frac{1}{2}[\hat{P}, [\hat{P}, \hat{\Omega}]] - \frac{i}{6}[\hat{P}, [\hat{P}, [\hat{P}, \hat{\Omega}]]] + \dots$$

- (a) Convince yourself that all contributions to the Hessian stem from the third term in the BCH expansion.
 - (b) Convince yourself that all off-diagonal elements of the Hessian are zero.
 - (c) Determine the matrix elements on the diagonal. You should here be able to identify excitation energies.
5. Property gradients have the structure

$$V^{[1]} = \begin{bmatrix} g \\ -g^* \end{bmatrix}$$

where the elements of the block vectors equal

$$g_n = \langle 0 | \left[|0\rangle \langle n|, \hat{V}^\omega \right] |0\rangle$$

Further, with an overlap matrix defined as

$$S^{[2]} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

show that the polarizability can be written

$$\alpha(\omega) = -\left[\Omega^{[1]} \right]^\dagger \left(E^{[2]} - \hbar\omega S^{[2]} \right)^{-1} V^{[1]}$$

Note: This matrix form of the polarizability thus embeds both terms in the sum-over-states expression. It is identical in form to expressions implemented for several approximate-state approaches, amongst them time-dependent DFT. The key difference in TDDFT is that the Hessian is not diagonal but instead becomes a diagonal-dominant matrix with orbital energy differences appearing on the diagonal.