Molecular properties lecture notes

1 Introduction

We have the time-independent electronic Schrödinger equation (SE):

$$\hat{H}_0 \Psi_n = E_n \Psi_n \tag{1}$$

where $\hat{H}_0$ is the Hamiltonian describing the isolated (unperturbed) system. When exposed to an external time-dependent field, the system responds and is now described by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \tag{2}$$

where the time-dependent term $\hat{V}(t)$ describes the quantum mechanical field-coupling, that is, the coupling between the molecular system and the external field. The perturbation term can be written in the form

$$\hat{V}(t) = \sum_{\omega} \hat{V}^{\omega} F^{\omega}(t) \tag{3}$$

where $\hat{V}^{\omega}$ is the coupling operator, $F^{\omega}(t)$ is the field amplitude, and ω is the frequency of the field. The sum runs over both positive and negative frequencies.

As a result of this time-dependence of the field, the eigenstates of the Hamiltonian are also time-dependent, and we are dealing with the time-dependent SE:

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}\Psi(t) = \left(\hat{H}_0 + \hat{V}(t)\right)\Psi(t) \tag{4}$$

and the expectation value of an operator ($\hat{\Omega}$) associated with an observable is time-dependent:

$$\Omega(t) = \langle \Psi(t) | \hat{\Omega} | \Psi(t) \rangle \tag{5}$$

In response theory, this expectation value is Fourier expanded in orders of the field, and the expansion coefficients define the response function to a given order:

$$\langle \Psi(t) | \hat{\Omega} | \Psi(t) \rangle = \langle 0 | \hat{\Omega} | 0 \rangle + \sum_{\omega} \left\langle\!\left\langle \hat{\Omega}; \hat{V} \right\rangle\!\right\rangle_{\omega} F^{\omega} \mathrm{e}^{-i\omega t} + \sum_{\omega_1,\omega_2} \left\langle\!\left\langle \hat{\Omega}; \hat{V}_1, \hat{V}_2 \right\rangle\!\right\rangle_{\omega_1,\omega_2} F^{\omega_1} F^{\omega_2} \mathrm{e}^{-i(\omega_1+\omega_2)t} + \ldots \tag{6}$$

The *linear response function* is defined as the coefficient of the expansion term which is linearly dependent on the perturbation, namely $\left\langle\!\left\langle \hat{\Omega}; \hat{V} \right\rangle\!\right\rangle_{\omega}$. The meaning of the double-brackets in this notation is unknown to the author of these notes. Note that this definition of the linear response function does not tell us anything about *how* the property is calculated, i.e., the analytical formulation. This is purely a property-defining expansion. The explicit formula depends on the chosen parametrization of $\Psi(t)$. The derivation of the sum-over-states expression of the linear response function for exact-state theory is available in this document.

In the electric dipole approximation, the magnetic field and higher-order electric interactions with the external field are ignored, and the perturbation operator is then defined as negative the dipole moment operator

$$\hat{V}(t) = -\mu F(t) \tag{7}$$

With this perturbation ($\hat{V} = -\hat{\mu}$) and the dipole moment as observable ($\hat{\Omega} = \hat{\mu}$), the linear response function is the electric dipole–electric dipole polarizability

$$\alpha_{\alpha\beta}(\omega) = -\left\langle\!\left\langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta} \right\rangle\!\right\rangle_{\omega} \tag{8}$$

where subscripts α and β denotes the cartesian coordinates of the tensors. Evidently, the polarizability is a two-dimensional tensor. The isotropic average of the polarizability is determined as the average of the diagonal elements

$$\bar{\alpha}(\omega) = \frac{1}{3}(\alpha_{xx}(\omega) + \alpha_{yy}(\omega) + \alpha_{zz}(\omega)) \ . \tag{9}$$

2 Exact state theory: sum-over-states expression for the linear response function

The analytic expression for a response function can be obtained via perturbation theory. For exact-state theory, i.e., where we have the complete set of exact eigenstates of the unperturbed Hamiltonian

$$\hat{H}_0 \left|n\right\rangle = E_n \left|n\right\rangle \tag{10}$$

the linear response function has the form of a sum-over-states (SOS):

$$\left\langle\left\langle \hat{\Omega}; \hat{V} \right\rangle\right\rangle_\omega = -\sum_n \left[\frac{\langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}|0\rangle}{\omega_{n0} - \omega} + \frac{\langle 0|\hat{V}|n\rangle \langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega} \right] \tag{11}$$

with $\omega_{n0} = E_n - E_0$.

This response function has poles when the frequency of the field, ω, is resonant with an electronic excitation in the system. We can find the strength of a given $0 \rightarrow n$ electronic transition from the residue of the linear response function:

$$\lim_{\omega \rightarrow \omega_{n0}} (\omega_{n0} - \omega) \left(-\sum_n \left[\frac{\langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}|0\rangle}{\omega_{n0} - \omega} + \frac{\langle 0|\hat{V}|n\rangle \langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega} \right] \right) = \langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}|0\rangle \tag{12}$$

where $\langle 0|\hat{\Omega}|n\rangle$ and $\langle n|\hat{V}|0\rangle$ are so-called transition moments.

2.1 Derivation of sum-over-states

The goal is to determine an expression that relates the molecular properties to other known parameters such as excitation energies and transition moments. We here do this with algebraic, perturbational solutions to the time-dependent SE, Eq. (4).

We have

$$\hat{V}(t) = \sum_\omega \hat{V}^\omega F^\omega(t) = \sum_\omega \hat{V}^\omega_\alpha F^\omega_\alpha \mathrm{e}^{-i\omega t} \mathrm{e}^{\epsilon t} \tag{13}$$

with implicit summation over repeated cartesian indices of the field ($\alpha \in x, y, z$). The parameter ϵ has the role of "turning off" the field in the time before the system was exposed to the external field, $\exp(\epsilon t) = 0$ for $t = -\infty$. We have the initial condition that the wavefunction describing the unperturbed system has the form

$$\Psi(t) = \Psi_n \mathrm{e}^{-iE_n t} \quad \text{for } t = -\infty \ . \tag{14}$$

Ψ_n is time-independent and we choose the reference state $n = 0$, i.e., the ground state of the unperturbed system. Furthermore,

$$F^{-\omega}_\alpha = [F^\omega_\alpha]^* \ , \tag{15}$$

$$\hat{V}^{-\omega}_\alpha = [\hat{V}^\omega_\alpha]^\dagger = \hat{V}^\omega_\alpha \ . \tag{16}$$

Now, we choose a parametrization of our wavefunction to start the derivation of the explicit response function. We choose a linear parametrization:

$$\left|\Psi(t)\right\rangle = \sum_n d_n(t) \mathrm{e}^{-iE_n t} \left|n\right\rangle \tag{17}$$

where n runs over the complete set of exact eigenstates.

Substitute the wave function into the time-dependent SE and project onto state $\langle m|$

$$i\frac{\partial}{\partial t} \sum_n \langle m| d_n(t) \mathrm{e}^{-iE_n t} \left|n\right\rangle = \sum_n \langle m| (\hat{H}_0 + \hat{V}(t)) d_n(t) \mathrm{e}^{-iE_n t} \left|n\right\rangle \tag{18}$$

Simplifying the left-hand-side

$$i\frac{\partial}{\partial t}\sum_n \langle m|\, d_n(t)\mathrm{e}^{-iE_nt}\,|n\rangle = i\frac{\partial}{\partial t}\sum_n \langle m|n\rangle\, d_n(t)\mathrm{e}^{-iE_nt} = i\frac{\partial}{\partial t}\sum_n \delta_{mn}d_n(t)\mathrm{e}^{-iE_nt} \tag{19}$$

$$= i\frac{\partial}{\partial t}\left(d_m(t)\mathrm{e}^{-iE_mt}\right) = i\frac{\partial d_m(t)}{\partial t}\,\mathrm{e}^{-iE_mt} + id_m(t)\frac{\partial}{\partial t}\mathrm{e}^{-iE_mt} \tag{20}$$

$$= i\frac{\partial d_m(t)}{\partial t}\,\mathrm{e}^{-iE_mt} + E_md_m(t)\mathrm{e}^{-iE_mt} \tag{21}$$

where we employed the product rule for derivatives. For the right-hand-side, we write

$$\sum_n \langle m|\,(\hat{H}_0+\hat{V}(t))d_n(t)\mathrm{e}^{-iE_nt}\,|n\rangle = \sum_n\left[\langle m|\hat{H}_0|n\rangle\, d_n(t)\mathrm{e}^{-iE_nt} + \langle m|\hat{V}(t)|n\rangle\, d_n(t)\mathrm{e}^{-iE_nt}\right] \tag{22}$$

$$= \sum_n\left[E_n\,\langle m|n\rangle\, d_n(t)\mathrm{e}^{-iE_nt} + V_{mn}(t)d_n(t)\mathrm{e}^{-iE_nt}\right] \tag{23}$$

$$= E_md_m(t)\mathrm{e}^{-iE_mt} + \sum_n V_{mn}(t)d_n(t)\mathrm{e}^{-iE_nt} \tag{24}$$

where the matrix element of the $\hat{V}$ operator has been introduced

$$V_{mn}(t) = \langle m|\hat{V}(t)|n\rangle\ . \tag{25}$$

We now have

$$i\frac{\partial d_m(t)}{\partial t}\,\mathrm{e}^{-iE_mt} + E_md_m(t)\mathrm{e}^{-iE_mt} = E_md_m(t)\mathrm{e}^{-iE_mt} + \sum_n V_{mn}(t)d_n(t)\mathrm{e}^{-iE_nt} \tag{26}$$

and by subtracting $E_md_m(t)\mathrm{e}^{-iE_mt}$ and multiplying by e^{iE_mt}, we get

$$i\frac{\partial d_m(t)}{\partial t} = \sum_n V_{mn}(t)d_n(t)\mathrm{e}^{i(E_m-E_n)t} \tag{27}$$

Now we use time-dependent perturbation theory to expand the d_n coefficients in orders of perturbation. First, we introduce a small unit-free parameter, λ, in the Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}(t)\ . \tag{28}$$

Then, we expand $d_n(t)$ in powers of λ

$$d_n(t) = d_n^{(0)}(t) + \lambda d_n^{(1)}(t) + \lambda^2 d_n^{(2)}(t) + ... \tag{29}$$

Substitute into Eq. (27)

$$i\frac{\partial}{\partial t}\left(d_n^{(0)}(t) + \lambda d_n^{(1)}(t) + \lambda^2 d_n^{(2)}(t) + ...\right) \tag{30}$$

$$= \sum_n \lambda V_{mn}(t)\left(d_n^{(0)}(t) + \lambda d_n^{(1)}(t) + \lambda^2 d_n^{(2)}(t) + ...\right)\mathrm{e}^{i(E_m-E_n)t} \tag{31}$$

$$= \sum_n V_{mn}(t)\left(\lambda d_n^{(0)}(t) + \lambda^2 d_n^{(1)}(t) + \lambda^3 d_n^{(2)}(t) + ...\right)\mathrm{e}^{i(E_m-E_n)t} \tag{32}$$

where the λ parameter in front of $V_{mn}(t)$ follows from using the Hamiltonian of Eq. (28) to derive Eq. (27). Now collect the terms that are in the same power of λ (and set $\lambda = 1$)

$$i\frac{\partial}{\partial t}d_n^{(0)}(t) = 0 \tag{33}$$

$$i\frac{\partial}{\partial t}d_n^{(1)}(t) = \sum_n V_{mn}(t)d_n^{(0)}(t)\mathrm{e}^{-i(Em-E_n)t} \tag{34}$$

$$\vdots \tag{35}$$

We see a pattern, and with time-integration we obtain the expression for the perturbation correction coefficient of order N

$$d_m^{(N)}(t) = \frac{1}{i}\int_{-\infty}^{t} \sum_n V_{mn}(t') d_n^{(N-1)}(t')\, \mathrm{e}^{i(E_m - E_n)t'} dt' \tag{36}$$

Expanding the wave function as

$$|\Psi(t)\rangle = |\Psi^{(0)}(t)\rangle + |\Psi^{(1)}(t)\rangle + |\Psi^{(2)}(t)\rangle + ... \tag{37}$$

we can write the general expression to the Nth order wave function

$$|\Psi^{(N)}(t)\rangle = \sum_n d_n^{(N)}(t) e^{-iE_n t} |n\rangle \tag{38}$$

The zeroth order perturbation correction to the wavefunction, $\Psi^{(0)}(t)$, is the unperturbed reference defined previously as an initial condition for our derivation. This initial condition translates into

$$d_n^0(t) = \delta_{n0} \tag{39}$$

such that

$$\Psi^{(0)}(t) = \sum_n d_n^{(0)}(t) e^{-iE_n t} |n\rangle = \sum_n \delta_{n0} e^{-iE_n t} |n\rangle = e^{-iE_0 t} |0\rangle \ . \tag{40}$$

To get the first-order correction to the wavefunction, first recall Eqs. (13) and (25). Then, for $N = 1$

$$d_m^{(1)}(t) = \frac{1}{i}\int_{-\infty}^{t} \sum_n \sum_\omega \langle m|\hat{V}_\alpha^\omega F_\alpha^\omega \mathrm{e}^{-i\omega t'} \mathrm{e}^{\epsilon t'} |n\rangle\, d_n^{(0)}(t')\, \mathrm{e}^{i(E_m - E_n)t'} dt' \tag{41}$$

$$= \frac{1}{i}\int_{-\infty}^{t} \sum_n \sum_\omega \langle m|\hat{V}_\alpha^\omega F_\alpha^\omega \mathrm{e}^{-i\omega t'} \mathrm{e}^{\epsilon t'} |n\rangle\, \delta_{n0}\, \mathrm{e}^{i(E_m - E_n)t'} dt' \tag{42}$$

$$= \frac{1}{i} \sum_\omega \frac{\langle m|\hat{V}_\alpha^\omega|0\rangle}{-i\omega + \epsilon + i\omega_{m0}} F_\alpha^\omega \mathrm{e}^{-i\omega t} \mathrm{e}^{\epsilon t} \mathrm{e}^{i(E_m - E_0)t} \tag{43}$$

$$= -\sum_\omega \frac{\langle m|\hat{V}_\alpha^\omega|0\rangle}{\omega_{m0} - \omega - i\epsilon} F_\alpha^\omega \mathrm{e}^{-i\omega t} \mathrm{e}^{\epsilon t} \mathrm{e}^{i(E_m - E_0)t} \tag{44}$$

The values at limit $t = -\infty$ disappear due to the ϵ exponential. We have

$$|\Psi^{(0)}(t)\rangle = |0\rangle\, \mathrm{e}^{-iE_0 t} \ , \tag{45}$$

$$|\Psi^{(1)}(t)\rangle = -\sum_n \sum_\omega \frac{\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0} - \omega - i\epsilon} F_\alpha^\omega \mathrm{e}^{-i\omega t} \mathrm{e}^{\epsilon t} \mathrm{e}^{i(E_n - E_0)t}\, \mathrm{e}^{-iE_n t} |n\rangle \ . \tag{46}$$

Now substitute the perturbation expansion of the wave function into the expectation value of operator $\hat{\Omega}$ (Eq. (5))

$$\langle\Psi(t)|\hat{\Omega}|\Psi(t)\rangle = \langle\Psi^{(0)}(t)|\hat{\Omega}|\Psi^{(0)}(t)\rangle + \langle\Psi^{(0)}(t)|\hat{\Omega}|\Psi^{(1)}(t)\rangle + \langle\Psi^{(1)}(t)|\hat{\Omega}|\Psi^{(0)}(t)\rangle + \langle\Psi^{(0)}(t)|\hat{\Omega}|\Psi^{(2)}(t)\rangle + ... \tag{47}$$

collect the terms linear in the perturbation

$$\langle\hat{\Omega}^{(1)}\rangle = \langle\Psi^{(0)}(t)|\hat{\Omega}|\Psi^{(1)}(t)\rangle + \langle\Psi^{(1)}(t)|\hat{\Omega}|\Psi^{(0)}(t)\rangle \tag{48}$$

and insert the wave function corrections (Eqs. (45), (46))

$$\langle\hat{\Omega}^{(1)}\rangle = -\langle 0|\,\mathrm{e}^{iE_0t}\hat{\Omega}\sum_n\sum_\omega\frac{\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0}-\omega-i\epsilon}F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t}\mathrm{e}^{i(E_n-E_0)t}\,\mathrm{e}^{-iE_nt}\,|n\rangle \tag{49}$$

$$-\sum_n\sum_\omega\frac{\langle 0|[\hat{V}_\alpha^\omega]^\dagger|n\rangle}{\omega_{m0}-\omega+i\epsilon}[F_\alpha^\omega]^*\mathrm{e}^{i\omega t}\mathrm{e}^{\epsilon t}\mathrm{e}^{-i(E_n-E_0)t}\,\mathrm{e}^{iE_nt}\,\langle n|\,\hat{\Omega}\mathrm{e}^{-iE_0t}\,|0\rangle \tag{50}$$

$$=-\sum_n\sum_\omega\frac{\langle 0|\hat{\Omega}|n\rangle\,\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0}-\omega-i\epsilon}\mathrm{e}^{iE_0t}F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t}\mathrm{e}^{i(E_n-E_0)t}\,\mathrm{e}^{-iE_nt} \tag{51}$$

$$-\sum_n\sum_\omega\frac{\langle 0|[\hat{V}_\alpha^\omega]^\dagger|n\rangle\,\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}-\omega+i\epsilon}[F_\alpha^\omega]^*\mathrm{e}^{i\omega t}\mathrm{e}^{\epsilon t}\mathrm{e}^{-i(E_n-E_0)t}\,\mathrm{e}^{iE_nt}\mathrm{e}^{-iE_0t} \tag{52}$$

$$=-\sum_n\sum_\omega\frac{\langle 0|\hat{\Omega}|n\rangle\,\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0}-\omega-i\epsilon}F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t} \tag{53}$$

$$-\sum_n\sum_\omega\frac{\langle 0|\hat{V}_\alpha^{-\omega}|n\rangle\,\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}-\omega+i\epsilon}F_\alpha^{-\omega}\mathrm{e}^{i\omega t}\mathrm{e}^{\epsilon t} \tag{54}$$

In the last term, we used that $F_\alpha^{-\omega}=[F_\alpha^\omega]^*$ and $\hat{V}_\alpha^{-\omega}=[\hat{V}_\alpha^\omega]^\dagger=\hat{V}_\alpha^\omega$. Now recalling that the sum over ω includes both positive and negative frequencies, we rewrite the last term and get

$$\langle\hat{\Omega}^{(1)}\rangle = -\sum_n\sum_\omega\frac{\langle 0|\hat{\Omega}|n\rangle\,\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0}-\omega-i\epsilon}F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t} \tag{55}$$

$$-\sum_n\sum_\omega\frac{\langle 0|\hat{V}_\alpha^\omega|n\rangle\,\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}+\omega+i\epsilon}F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t} \tag{56}$$

$$=-\sum_\omega\sum_n\left[\frac{\langle 0|\hat{\Omega}|n\rangle\,\langle n|\hat{V}_\alpha^\omega|0\rangle}{\omega_{n0}-\omega-i\epsilon}+\frac{\langle 0|\hat{V}_\alpha^\omega|n\rangle\,\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}+\omega+i\epsilon}\right]F_\alpha^\omega\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t}\ . \tag{57}$$

It is noted that $i\epsilon$ is small and can for most practical purposes be set to zero. Comparing Eq. (57) with Eq. (6) we see that we have indeed obtained the sum-over-states expression for the linear response function provided in Eq. (11).

3 Hartree–Fock: random phase approximation matrix formulation

In the self-consistent field methods HF and DFT, the linear response function can be derived and formulated in a matrix-vector form, called the random phase approximation (for historical reasons):

$$\langle\langle\hat{\Omega};\hat{V}\rangle\rangle_\omega=[\Omega^{[1]}]^\dagger(E^{[2]}-\omega S^{[2]})^{-1}V^{\omega,[1]}\ . \tag{58}$$

Here, $\Omega^{[1]}$ and $V^{\omega,[1]}$ are the so-called property gradients with the general form

$$G=\begin{pmatrix}g\\-g^*\end{pmatrix} \tag{59}$$

where $\mathbf{g}$ is basically just the MO-transformation of a general operator $\hat{g}$. A property gradient is a column vector of length $2n_{occ}n_{vir}$. Meanwhile, $E^{[2]}$ is the electronic Hessian defined as

$$E^{[2]}=\begin{pmatrix}A&B\\B^*&A^*\end{pmatrix} \tag{60}$$

where A and B are a common notation for the matrices with elements

$$A_{ai,bj} = F_{ab}\delta_{ij} - F_{ji}\delta_{ab} - \langle aj||bi\rangle \ , \tag{61}$$

$$B_{ai,bj} = -\langle ab||ij\rangle \ , \tag{62}$$

$$F_{pq} = h_{pq} + \sum_{i}^{occ} \langle pi||qi\rangle \ . \tag{63}$$

Here, *a, b* are indices for virtual orbitals, *i, j* for occupied, and *p, q* are general orbital indices. The electronic Hessian is then a two-dimensional matrix with dimensions $2n_{occ}n_{vir} \times 2n_{occ}n_{vir}$. The overlap matrix $S^{[2]}$ is defined as

$$S^{[2]} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{64}$$

where I is to be understood as the identity matrix with dimensions $n_{occ}n_{vir} \times n_{occ}n_{vir}$. $S^{[2]}$ then has the same dimensions as the Hessian.

Let n specify the number of excited states of a molecular system and $e = -n, ..., -1, 1, ..., n$. From the generalized eigenequation

$$E^{[2]}X_e = \lambda_e S^{[2]}X_e \tag{65}$$

we can determine the eigenvalues and -vectors by diagonalizing the $[S^{[2]}]^{-1}E^{[2]}$ matrix

$$X^{-1}[S^{[2]}]^{-1}E^{[2]}X = \begin{pmatrix} \lambda & 0 \\ 0 & -\lambda \end{pmatrix} \ . \tag{66}$$

Here, λ is a diagonal matrix containing all positive eigenvalues with dimensions $n \times n$ and X is a matrix with each column being an eigenvector and dimensions $n_{occ}n_{vir} \times n$. For the eigenvectors we have

$$X_e = \begin{pmatrix} Z_e \\ Y_e^* \end{pmatrix} \quad \text{with eigenvalue } \lambda_e \ , \tag{67}$$

$$X_{-e} = \begin{pmatrix} Y_e \\ Z_e^* \end{pmatrix} \quad \text{with eigenvalue } -\lambda_e \ . \tag{68}$$

Z and Y are referred to as the excitation and de-excitation vectors, respectively.

We now want to reshape Eq. (58) in a sum-over-states form to resemble the one derived for exact states. For this, we need the following information: with an appropriate scaling of X, we have that

$$X^\dagger E^{[2]}X = \begin{pmatrix} \lambda & 0 \\ 0 & \lambda \end{pmatrix} \ , \tag{69}$$

$$X^\dagger S^{[2]}X = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \ . \tag{70}$$

We now reformulate the inverse matrix in Eq. (58) as

$$(E^{[2]} - \omega S^{[2]})^{-1} = X\left[X^\dagger(E^{[2]} - \omega S^{[2]})X\right]^{-1}X^\dagger \tag{71}$$

and start our translation into a sum-over-states expression

$$X\left[X^\dagger(E^{[2]} - \omega S^{[2]})X\right]^{-1}X^\dagger = X\left[X^\dagger E^{[2]}X - \omega X^\dagger S^{[2]}X\right]^{-1}X^\dagger \tag{72}$$

$$= X\left[\begin{pmatrix} \lambda & 0 \\ 0 & \lambda \end{pmatrix} - \omega\begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}\right]^{-1}X^\dagger = X\Lambda^{-1}X^\dagger \tag{73}$$

where we have introduced the diagonal Λ matrix which we assume to be invertible

$$\Lambda = \begin{pmatrix} \lambda - \omega I & 0 \\ 0 & \lambda + \omega I \end{pmatrix} . \tag{74}$$

The RPA now has the form

$$[\Omega^{[1]}]^\dagger (E^{[2]} - \omega S^{[2]})^{-1} V^{\omega,[1]} = [\Omega^{[1]}]^\dagger X \Lambda^{-1} X^\dagger V^{\omega,[1]} \tag{75}$$

Since matrix multiplication is associative, i.e., $(AB)C = A(BC)$ we can choose to consider first the $X\Lambda^{-1}X^\dagger$ bit. We recognize that the multiplication of a given matrix B with a diagonal matrix A results in the rows of B being scaled by the corresponding diagonal element in A. That is, all elements in the first row of B is scaled by the first diagonal element of A etc. Thus,

$$\Lambda^{-1} X^\dagger = \begin{pmatrix} (\lambda_1 - \omega)^{-1} X_1^\dagger \\ \vdots \\ (\lambda_n - \omega)^{-1} X_n^\dagger \\ (\lambda_1 + \omega)^{-1} X_{-1}^\dagger \\ \vdots \\ (\lambda_{-n} + \omega)^{-1} X_{-n}^\dagger \end{pmatrix} . \tag{76}$$

Matrix multiplication with X on the left then looks as follows

$$X\Lambda^{-1}X^\dagger = \begin{pmatrix} | & \dots & | & | & \dots & | \\ X_1 & \dots & X_n & X_{-1} & & X_{-n} \\ | & \dots & | & | & \dots & | \\ & & & & & \end{pmatrix} \begin{pmatrix} (\lambda_1 - \omega)^{-1} X_1^\dagger \\ \vdots \\ (\lambda_n - \omega)^{-1} X_n^\dagger \\ (\lambda_1 + \omega)^{-1} X_{-1}^\dagger \\ \vdots \\ (\lambda_{-n} + \omega)^{-1} X_{-n}^\dagger \end{pmatrix} \tag{77}$$

The result will be a vector with elements

$$\sum_{e=1}^{n} \sum_{i}^{2n_{occ}n_{vir}} (\lambda_e - \omega)^{-1} X_{e,i} X_{e,i}^* + \sum_{e=-n}^{-1} \sum_{i}^{2n_{occ}n_{vir}} (\lambda_e + \omega)^{-1} X_{e,i} X_{e,i}^* \tag{78}$$

$$= \sum_{e=1}^{n} \sum_{i}^{n_{occ}n_{vir}} (\lambda_e - \omega)^{-1} [Z_{e,i} Z_{e,i}^* + Y_{e,i}^* Y_{e,i}] + \sum_{e=1}^{n} \sum_{i}^{n_{occ}n_{vir}} (\lambda_e + \omega)^{-1} [Y_{e,i} Y_{e,i}^* + Z_{e,i}^* Z_{e,i}] \tag{79}$$

$$= \sum_{e=1}^{n} \frac{X_e X_e^\dagger}{\lambda_e - \omega} + \frac{X_e X_e^\dagger}{\lambda_e + \omega} \tag{80}$$

Inserting this into Eq. (58) we get

$$\langle\langle \hat{\Omega}; \hat{V} \rangle\rangle_\omega = [\Omega^{[1]}]^\dagger \sum_{e=1}^{n} \left[\frac{X_e X_e^\dagger}{\lambda_e - \omega} + \frac{X_e X_e^\dagger}{\lambda_e + \omega} \right] V^{\omega,[1]} \tag{81}$$

and the resemblance of the exact-state response function is evident. We identify

$$\omega_{n0} = \lambda_e , \tag{82}$$

$$\langle 0 | \hat{\Omega} | n \rangle = [\Omega^{[1]}]^\dagger X_e , \tag{83}$$

$$\langle n | \hat{V}^\omega | 0 \rangle = X_e^\dagger V^{\omega,[1]} . \tag{84}$$