9 Response theory

Remark 9.1. In the presence of a time-varying field, the electronic wavefunction is no longer simply an eigenfunction of the Hamiltonian. Instead, the electronic structure is described by the *time-dependent Schrödinger equation*

$$H(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t} \qquad H(t) = H + V(t) \tag{9.1}$$

where H is the usual electronic Hamiltonian and the *interaction Hamiltonian* $V(t)$ describes electronic coupling to the external field. Most interactions can be expressed as a sum over one-electron operators V_β representing the electronic degrees of freedom which are coupled to the field, scaled by *time-envelopes* $f_\beta(t)$ representing the field strength over time.

$$V(t) = \sum_\beta V_\beta f_\beta(t) \tag{9.2}$$

where $\{V_\beta\}$ is a set of one-electron operators

$V(t)$ is a time-dependent perturbation describing the energetic coupling to the .

the time-dependent perturbation $V(t)$ is the Hamiltonian of the interaction between the electrons and the time-varying field.

Remark 9.2. In the presence of a time-varying field, the electronic wavefunction is no longer simply an eigenfunction of the Hamiltonian. This more general system is described by the following *time-dependent Schrödinger equation* where H is the usual electronic Hamiltonian and $V(t)$ describes the interaction with the external field.
Appendix A shows how to solve this.

A convenient starting point for *response theory* is to cast the interaction Hamiltonian in the following form

$$V(t) = \textstyle\sum_\beta V_\beta f_\beta(t) \tag{9.3}$$

where $\{V_\beta\}$ is a set of one-particle operators and the $f_\beta(t)$'s are scalar-valued *time envelopes*. A convenient set of boundary conditions for response theory turns the interaction off in the infinite past and requires that the system begins in a stationary state, which is usually chosen to be the ground state.

$$\lim_{t\to-\infty} f_\beta(t) = 0 \qquad \lim_{t\to-\infty} \tilde{\Psi}(t) = \Psi_0 \qquad H\Psi_k = E_k\Psi_k \tag{9.4}$$

This can be imposed on any time envelope with a finite $t \to -\infty$ limit by building in a factor $e^{-\epsilon t}$ where ϵ is a real number. For sufficiently small ϵ, this new envelope will match the old one to arbitrary precision in an arbitrarily wide window about the time origin.

Example 9.1. ***The dipole approximation.*** The dominant coupling of an electronic system to an external electric or magnetic field, $\mathbf{E}(t)$ or $\mathbf{B}(t)$, is mediated through its dipoles. Quantizing the classical formulae for these interactions gives

$$\begin{array}{lll} V_{\mathbf{E}}(t) \approx -\boldsymbol{\mu}\cdot\mathbf{E}(t) = -\sum_\beta \mu_\beta \mathcal{E}_\beta(t) & \boldsymbol{\mu} = \sum_{pq}\langle\psi_p|\hat{\boldsymbol{\mu}}|\psi_q\rangle a_p^\dagger a_q & \hat{\boldsymbol{\mu}} = -\hat{\mathbf{r}} \\ V_{\mathbf{B}}(t) \approx -\boldsymbol{m}\cdot\mathbf{B}(t) = -\sum_\beta m_\beta \mathcal{B}_\beta(t) & \boldsymbol{m} = \sum_{pq}\langle\psi_p|\hat{\boldsymbol{m}}|\psi_q\rangle a_p^\dagger a_q & \hat{\boldsymbol{m}} = -\frac{1}{2}(\hat{\boldsymbol{l}} + 2\,\hat{\mathbf{s}}) \end{array} \tag{9.5}$$

where $\hat{\boldsymbol{\mu}}$ and $\hat{\boldsymbol{m}}$ are the first-quantized electric and magnetic dipole operators of a single electron.[1] The orbital angular momentum operator is $\hat{\boldsymbol{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$, and $\hat{\mathbf{s}}$ is the intrinsic spin angular momentum operator.

Definition 9.1. ***Quasi-energy.***

$$\Psi(t) = e^{-i\theta(t)}\bar{\Psi}(t) \qquad \lim_{t\to-\infty}\bar{\Psi}(t) = \Psi_0 \qquad \theta(t)|_{\boldsymbol{f}=\mathbf{0}} = E_0 t \tag{9.6}$$

$$(H(t) - i\tfrac{\partial}{\partial t})\bar{\Psi}(t) = \dot{\theta}(t)\bar{\Psi}(t) \tag{9.7}$$

$$\dot{\theta}(t) = \int_0^t dt' \langle\bar{\Psi}(t')|H(t') - i\tfrac{\partial}{\partial t'}|\bar{\Psi}(t')\rangle \tag{9.8}$$

$$\langle\delta\bar{\Psi}(t)|H(t) - i\tfrac{\partial}{\partial t}|\bar{\Psi}(t)\rangle = \dot{\theta}(t)\langle\delta\bar{\Psi}(t)|\bar{\Psi}(t)\rangle \tag{9.9}$$

$$\langle\delta\bar{\Psi}(t)|\bar{\Psi}(t)\rangle + \langle\bar{\Psi}(t)|\delta\bar{\Psi}(t)\rangle = 0 \tag{9.10}$$

$$\delta\langle\bar{\Psi}(t)|H(t) - i\tfrac{\partial}{\partial t}|\bar{\Psi}(t)\rangle + i\tfrac{\partial}{\partial t}\langle\bar{\Psi}(t)|\delta\bar{\Psi}(t)\rangle = 0 \tag{9.11}$$

[1] More generally, these expressions are $\hat{\boldsymbol{\mu}} = q_e\,\hat{\mathbf{r}}$, where $q_e = -e$ is the charge of an electron, and $\hat{\boldsymbol{m}} = \mu_{\mathrm{B}}(g_l\,\hat{\boldsymbol{l}} + g_{\mathrm{s}}\,\hat{\mathbf{s}})$ where $\mu_{\mathrm{B}} = \frac{1}{2}\cdot\frac{e\hbar}{m_e}$ is the Bohr magneton and $g_l = -1$, $g_{\mathrm{s}} = -2$ are the spin and orbital *g-factors*. Note that the exact g_{s} actually deviates very slightly from 2 due to effects arising in quantum field theory.

A Time-dependent perturbation theory

Remark A.1. If the electrons are prepared in a particular state Ψ_0 at some time t_0, the system is completely described by a *time-evolution operator*.

$$\Psi(t) = U(t,t_0)\Psi_0 \qquad\qquad \Psi_0 = \Psi(t_0) \tag{A.1}$$

The following discussion shows how to expand this operator in orders of the perturbing interaction, $V(t)$.

Definition A.1. ***Interaction picture.*** The *interaction picture* results from to the following similarity transformation.

$$\tilde{\Theta}(t) \equiv e^{+iHt}\Theta(t) \qquad\qquad \tilde{W}(t) \equiv e^{+iHt}We^{-iHt} \tag{A.2}$$

Expanding the Schrödinger equation in the interaction picture yields the the *Schwinger-Tomonaga equation*.

$$\tilde{V}(t)\tilde{\Psi}(t) = i\frac{\partial\tilde{\Psi}(t)}{\partial t} \tag{A.3}$$

Multiplying both sides by $-i$ and integrating from t_0 to t yields a recursive equation for the interaction-picture wavefunction

$$\tilde{\Psi}(t) - \tilde{\Psi}(t_0) = -i\int_{t_0}^{t} dt'\,\tilde{V}(t')\tilde{\Psi}(t') \tag{A.4}$$

from which we infer $\tilde{U}(t,t_0) = 1 - i\int_{t_0}^{t} dt'\tilde{V}(t')\,\tilde{U}(t',t_0)$. Infinite recursion yields the following.

$$\tilde{U}(t,t_0) = \sum_{n=0}^{\infty}(-i)^n\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{n-1}}dt_n\,\tilde{V}(t_1)\cdots\tilde{V}(t_n) \tag{A.5}$$

Definition A.2. ***Time-ordering.*** Let $\tilde{q}_1(t_1)\cdots\tilde{q}_n(t_n)$ be a string of particle-hole operators in the interaction picture.[2] The *time-ordering map* takes this string into $\mathcal{T}\{\tilde{q}_1(t_1)\cdots\tilde{q}_n(t_n)\} \equiv \varepsilon_\pi\,\tilde{q}_{\pi(1)}(t_{\pi(1)})\cdots\tilde{q}_{\pi(n)}(t_{\pi(n)})$, where $\pi \in \mathrm{S}_n$ is a permutation that puts the time arguments in reverse-chronological order, $t_{\pi(1)} > \cdots > t_{\pi(n)}$.

Notation A.1. The following notation proves convenient for manipulating multiple integrals

$$\int_{t_1t_2t_3\cdots}^{[t_0,t]}dt_1dt_2dt_3\cdots \equiv \int_{t_0}^{t}dt_1\int_{t_0}^{t}dt_2\int_{t_0}^{t}dt_3\cdots \qquad \int_{t_1>t_2>t_3>\cdots}^{[t_0,t]}dt_1dt_2dt_3\cdots \equiv \int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\cdots \tag{A.6}$$

which is defined by analogy with summation notation $\sum_{i_1i_2i_3\cdots}^{\{n_0,\dots,n\}}$ and $\sum_{i_1>i_2>i_3\cdots}^{\{n_0,\dots,n\}}$. That is, the t_i's are dummy variables which we integrate over all values in $[t_0,t]$ satisfying a condition, such as $t_1 > t_2 > t_3 > \cdots$. Then the identity

$$\int_{t_1\cdots t_n}^{[t_0,t]}dt_1\cdots t_n\,f(t_1\cdots t_n) = \sum_{\pi}^{\mathrm{S}_n}\int_{t_{\pi(1)}>\dots>t_{\pi(n)}}^{[t_0,t]}dt_1\cdots t_n\,f(t_1\cdots t_n) \tag{A.7}$$

follows from considering all possible chronologies for $t_1,\dots,t_n$ in the unrestricted integral.[3][4]

Proposition A.1. ***The Dyson series.*** $\tilde{U}(t,t_0) = \mathcal{T}\{e^{-i\int_{t_0}^{t}dt'\,\tilde{V}(t')}\}$

Proof: Expanding the exponential in a Taylor series and applying equation A.7 gives the following

$$\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{t_1\cdots t_n}^{[t_0,t]}dt_1\cdots dt_n\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\} = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\sum_{\pi}^{\mathrm{S}_n}\int_{t_{\pi(1)}>\dots>t_{\pi(n)}}^{[t_0,t]}dt_1\cdots dt_n\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\} \tag{A.8}$$

which simplifies to equation A.5 because all $n!$ terms in the sum over π are equivalent by def A.2.[5]

Remark A.2. The Dyson series for the wavefunction can then be written in the form

$$\tilde{\Psi}(t) = \lim_{t_0\to-\infty}\tilde{U}(t,t_0)\Psi_0 = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{\mathbb{R}^n}dt_1\cdots dt_n\,\theta(t-t_1)\cdots\theta(t-t_n)\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\}\Psi_0 \tag{A.9}$$

where $\theta(x) = \int_{-\infty}^{x}dx'\delta(x')$ is the Heaviside step function, which here enforces an upper limit of t for each integral over t_i.

[2] As in $\tilde{q}(t) \equiv e^{+iHt}qe^{-iHt}$ for some $q \in \{a_p\} \cup \{a_p^\dagger\}$.

[4] The corresponding summation identity would be $\sum_{i_1\neq i_2\neq i_3\neq\cdots}^{\{n_0,n\}} = \sum_{\pi}^{\mathrm{S}_n}\sum_{i_{\pi(1)}>i_{\pi(2)}>i_{\pi(3)}>\cdots}^{\{n_0,n\}}$. The unrestricted integral is equivalent to an integral over $t_1 \neq t_2 \neq t_3 \neq \cdots$ because individual integrand values have "measure zero": $\int_{t_j}^{t_j}dt_i = 0$.

[5] We are assuming that $\tilde{V}(t)$ is particle-number-conserving, or at least contains only even operator products.

B Response functions

Definition B.1. Any perturbation-dependent quantity $X(t)$ can be expanded in a Taylor expansion of the time-envelopes

$$X(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{\beta_1,\ldots,\beta_n} \int_{\mathbb{R}^n} dt_1 \cdots t_n \, f_{\beta_1}(t_1) \cdots f_{\beta_n}(t_n) \, X^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n} \qquad X^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n} \equiv \left. \frac{d^n X(t)}{df_{\beta_1}(t_1) \cdots df_{\beta_n}(t_n)} \right|_{\boldsymbol{f}=\boldsymbol{0}} \tag{B.1}$$

where the coefficients $X^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n}$ are n^{th}-order *responses* of X. When the quantity of interest is an observable expectation value, $W(t) = \langle \Psi(t)|W|\Psi(t)\rangle$, we write $\langle\langle \tilde{W}(t); \tilde{V}_{\beta_1}(t_1), \ldots, \tilde{V}_{\beta_n}(t_n)\rangle\rangle \equiv W^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n}$. In some contexts, these *property response functions* are also known to as *retarded propagators* or *retarded Green's functions*. Note that, since W does not explicitly depend on time, shifting the time origin does not change the value of $W(t)$, because $U(t, t_0)$ only depends on the time elapsed between t_0 and t. This implies $\langle\langle \tilde{W}(t); \tilde{V}_{\beta_1}(t_1), \ldots, \tilde{V}_{\beta_n}(t_n)\rangle\rangle = \langle\langle \tilde{W}(0); \tilde{V}_{\beta_1}(\tau_1), \ldots, \tilde{V}_{\beta_n}(\tau_n)\rangle\rangle$ where we have shifted the origin to t and defined $\tau_j \equiv t_j - t$.

Example B.1. Substituting eq 9.3 into eq A.9 and comparing the result to eq B.1 yields the wavefunction responses.

$$\tilde{\Psi}^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n} = (-i)^n \theta(t - t_1) \cdots \theta(t - t_n) \, \mathcal{T}\{\tilde{V}_{\beta_1}(t_1) \cdots \tilde{V}_{\beta_n}(t_n)\} \Psi_0 \tag{B.2}$$

Substituting this expansion into $\langle \Psi(t)|W|\Psi(t)\rangle = \langle \tilde{\Psi}(t)|\tilde{W}(t)|\tilde{\Psi}(t)\rangle$ and grouping powers of $\boldsymbol{f}$ gives the following

$$\langle\langle \tilde{W}(t); \tilde{V}_{\beta_1}(t_1), \ldots, \tilde{V}_{\beta_n}(t_n)\rangle\rangle = \sum_{p=0}^{n} \frac{1}{p!(n-p)!} \sum_{\pi}^{\mathrm{S}_n} \langle \tilde{\Psi}^{\beta_{\pi(1)} \cdots \beta_{\pi(p)}}_{t;t_{\pi(1)} \cdots t_{\pi(p)}} |\tilde{W}(t)| \tilde{\Psi}^{\beta_{\pi(p+1)} \cdots \beta_{\pi(n)}}_{t;t_{\pi(p+1)} \cdots t_{\pi(n)}} \rangle \tag{B.3}$$

which can be further simplified using the permutational symmetries of the wavefunction responses.

Proposition B.1. $\langle\langle \tilde{W}(t); \tilde{V}_\beta(t')\rangle\rangle = -i\theta(t - t')\langle \Psi_0|[\tilde{W}(t), \tilde{V}_\beta(t')]|\Psi_0\rangle$

Proof: This follows from equations B.2 and B.3 with $n = 1$.

Corollary B.1. *Defining the excitation energy $\omega_k \equiv E_k - E_0$, the linear response function can be expressed as follows.*

$$\langle\langle \tilde{W}(t); \tilde{V}_\beta(t')\rangle\rangle = -i\theta(t - t') \sum_{k=0}^{\infty} (e^{-i\omega_k(t-t')} \langle \Psi_0|W|\Psi_k\rangle\langle \Psi_k|V_\beta|\Psi_0\rangle - e^{-i\omega_k(t'-t)} \langle \Psi_0|V_\beta|\Psi_k\rangle\langle \Psi_k|W|\Psi_0\rangle)$$

Proof: Expanding the interaction-picture operators of prop B.1 in the Schrödinger picture yields the following

$$\langle\langle \tilde{W}(t); \tilde{V}_\beta(t')\rangle\rangle = \; - i\theta(t - t')(\langle \Psi_0|W e^{-i(H-E_0)(t-t')} V_\beta|\Psi_0\rangle - \langle \Psi_0|V_\beta e^{-i(H-E_0)(t'-t)} W|\Psi_0\rangle) \tag{B.4}$$

where we have used $H\Psi_0 = E_0\Psi_0$. The proposition follows by inserting resolution of the identity

C Fourier transforms

Remark C.1. The time-envelopes of

Remark C.2.

$$f_\beta(t) = \int_{-\infty}^{\infty} d\omega\, f_\beta(\omega_\epsilon) e^{-i\omega_\epsilon t} \qquad f_\beta(\omega_\epsilon) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} dt\, f_\beta(t) e^{+i\omega_\epsilon t} \qquad \omega_\epsilon \equiv \omega + i\epsilon \tag{C.1}$$

$f_\beta(-\omega) = f_\beta^*(\omega)$

Footnote: Fourier transforms can always be verified using $\int_{\mathbb{R}} dk\, e^{ikx} = 2\pi\, \delta(x)$

Remark C.3. Define $\tau_j \equiv t_j - t$ and note that $X^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n} = X^{\beta_1 \cdots \beta_n}_{0;\tau_1 \cdots \tau_n}$

$$X^{\beta_1 \cdots \beta_n}_{0;\tau_1 \cdots \tau_n} \equiv (2\pi)^{-n} \int_{\mathbb{R}^n} d\omega_1 \cdots d\omega_n\, X^{\beta_1 \cdots \beta_n}_{\omega_{\epsilon,1} \cdots \omega_{\epsilon,n}} e^{+i\sum_j \omega_{\epsilon,j}\tau_j} \qquad X^{\beta_1 \cdots \beta_n}_{\omega_{\epsilon,1} \cdots \omega_{\epsilon,n}} \equiv \int_{\mathbb{R}^n} d\tau_1 \cdots d\tau_n\, X^{\beta_1 \cdots \beta_n}_{0;\tau_1 \cdots \tau_n} e^{-i\sum_j \omega_{\epsilon,j}\tau_j} \tag{C.2}$$

Remark C.4. $\int_{\mathbb{R}^n} dt_1 \cdots dt_n\, f_{\beta_1}(t_1) \cdots f_{\beta_n}(t_n)\, X^{\beta_1 \cdots \beta_n}_{t;t_1 \cdots t_n} = \int_{\mathbb{R}^n} d\omega_1 \cdots d\omega_n\, f_{\beta_1}(\omega_{\epsilon,1}) \cdots f_{\beta_n}(\omega_{\epsilon,n}) X^{\beta_1 \cdots \beta_n}_{\omega_{\epsilon,1} \cdots \omega_{\epsilon,n}} e^{-i\sum_j \omega_{\epsilon,j} t}$

$$\langle\langle \tilde{W}(t); \tilde{V}_\beta(t') \rangle\rangle = \sum_{k=0}^{\infty} (g_k^+(\tau) \langle \Psi_0 | W | \Psi_k \rangle \langle \Psi_k | V_\beta | \Psi_0 \rangle - g_k^-(\tau) \langle \Psi_0 | V_\beta | \Psi_k \rangle \langle \Psi_k | W | \Psi_0 \rangle) \quad g_k^\pm(\tau) \equiv -i\theta(-\tau) e^{\pm i\omega_k \tau} \tag{C.3}$$

$$g_k^\pm(\omega_\epsilon) = \int_{-\infty}^{\infty} d\tau\, g_k^\pm(\tau) e^{-i\omega_\epsilon \tau} = -i \int_{-\infty}^{0} d\tau\, e^{-i(\omega_\epsilon \mp \omega_k)\tau} = \frac{1}{\omega_\epsilon \mp \omega_k} \tag{C.4}$$

$$g_k^\pm(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, g_k^\pm(\omega_\epsilon) e^{+i\omega_\epsilon \tau} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, \frac{e^{+i\omega_\epsilon \tau}}{\omega_\epsilon \mp \omega_k} \tag{C.5}$$

D Complex Calculus