A Time-dependent perturbation theory

Remark A.1. In an 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*

$$H(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t} \qquad\qquad H(t) = H + V(t) \tag{A.1}$$

where H is the usual electronic Hamiltonian and $V(t)$ describes the interaction with the external field. 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*.

$$\Psi(t) = U(t,t_0)\Psi_0 \qquad\qquad \Psi_0 = \Psi(t_0) \tag{A.2}$$

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.

$$\tilde{\Theta}(t) \equiv e^{+iHt}\Theta(t) \qquad\qquad \tilde{W}(t) \equiv e^{+iHt}We^{-iHt} \tag{A.3}$$

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

$$\tilde{V}(t)\tilde{\Psi}(t) = i\frac{\partial\tilde{\Psi}(t)}{\partial t} \tag{A.4}$$

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

$$\tilde{\Psi}(t) - \tilde{\Psi}(t_0) = -i\int_{t_0}^{t} dt'\,\tilde{V}(t')\tilde{\Psi}(t') \tag{A.5}$$

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.

$$\tilde{U}(t,t_0) = \sum_{n=0}^{\infty}(-i)^n\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{n-1}}dt_n\,\tilde{V}(t_1)\cdots\tilde{V}(t_n) \tag{A.6}$$

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.[1] 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

$$\int_{t_1t_2t_3\cdots}^{[t_0,t]}dt_1dt_2dt_3\cdots \equiv \int_{t_0}^{t}dt_1\int_{t_0}^{t}dt_2\int_{t_0}^{t}dt_3\cdots \qquad \int_{t_1>t_2>t_3>\cdots}^{[t_0,t]}dt_1dt_2dt_3\cdots \equiv \int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\cdots \tag{A.7}$$

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

$$\int_{t_1\cdots t_n}^{[t_0,t]}dt_1\cdots t_n\,f(t_1\cdots t_n) = \sum_{\pi}^{\mathrm{S}_n}\int_{t_{\pi(1)}>\dots>t_{\pi(n)}}^{[t_0,t]}dt_1\cdots t_n\,f(t_1\cdots t_n) \tag{A.8}$$

follows from considering all possible chronologies for $t_1,\dots,t_n$ in the unrestricted integral.[2][3]

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.8 gives the following

$$\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{t_1\cdots t_n}^{[t_0,t]}dt_1\cdots dt_n\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\} = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\sum_{\pi}^{\mathrm{S}_n}\int_{t_{\pi(1)}>\dots>t_{\pi(n)}}^{[t_0,t]}dt_1\cdots dt_n\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\} \tag{A.9}$$

which simplifies to equation A.6 because all $n!$ terms in the sum over π are equivalent by def A.2.[4]

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

[3] 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": $\int_{t_j}^{t_j}dt_i = 0$.

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

B Response functions

Remark B.1. A convenient starting point for *response theory* is to cast the interaction Hamiltonian in the following form

$$V(t) = \textstyle\sum_\beta V_\beta f_\beta(t) \tag{B.1}$$

where $\{V_\beta\}$ is a set of one-particle operators and the $f_\beta(t)$'s are scalar-valued *time envelopes*.

Example B.1. Interactions with electric and magnetic fields are approximately described by the following Hamiltonians

$$\begin{aligned} V_{\mathbf{E}}(t) &= -\boldsymbol{\mu}\cdot\mathbf{E}(t) = -\textstyle\sum_\beta \mu_\beta \mathcal{E}_\beta(t) & \boldsymbol{\mu} &= \textstyle\sum_{pq}\langle\psi_p|\hat{\boldsymbol{\mu}}|\psi_q\rangle a_p^\dagger a_q & \hat{\boldsymbol{\mu}} &= -\hat{\mathbf{r}} \\ V_{\mathbf{B}}(t) &= -\boldsymbol{m}\cdot\mathbf{B}(t) = -\textstyle\sum_\beta m_\beta \mathcal{B}_\beta(t) & \boldsymbol{m} &= \textstyle\sum_{pq}\langle\psi_p|\hat{\boldsymbol{m}}|\psi_q\rangle a_p^\dagger a_q & \hat{\boldsymbol{m}} &= -\frac{\hat{\mathbf{r}}\times\hat{\mathbf{p}}}{2} \end{aligned} \tag{B.2}$$

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are the electric and magnetic dipole operators and the field components, $\mathcal{E}_\beta(t)$ and $\mathcal{B}_\beta(t)$, are scalar-valued functions of time. This is known as the *dipole approximation*.

Remark B.2. 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.

$$\lim_{t\to-\infty} f_\beta(t) = 0 \qquad \lim_{t\to-\infty}\tilde{\Psi}(t) = \Psi_0 \qquad H\Psi_k = E_k\Psi_k \tag{B.3}$$

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

$$\tilde{\Psi}(t) = \lim_{t_0\to-\infty}\tilde{U}(t,t_0)\Psi_0 = \sum_{n=0}^\infty \frac{(-i)^n}{n!}\int_{\mathbb{R}^n} dt_1\cdots dt_n\,\theta(t-t_1)\cdots\theta(t-t_n)\,\mathcal{T}\{\tilde{V}(t_1)\cdots\tilde{V}(t_n)\}\Psi_0 \tag{B.4}$$

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.

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

$$X(t) = \sum_{n=0}^\infty \frac{1}{n!}\sum_{\beta_1,\ldots,\beta_n}\int_{\mathbb{R}^n} dt_1\cdots t_n\, f_{\beta_1}(t_1)\cdots f_{\beta_n}(t_n)\, X_{t;t_1\cdots t_n}^{\beta_1\cdots\beta_n} \qquad X_{t;t_1\cdots t_n}^{\beta_1\cdots\beta_n} \equiv \left.\frac{d^nX(t)}{df_{\beta_1}(t_1)\cdots df_{\beta_n}(t_n)}\right|_{\boldsymbol{f}=\mathbf{0}} \tag{B.5}$$

where the coefficients $X_{t;t_1\cdots t_n}^{\beta_1\cdots\beta_n}$ 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 $\langle\langle\tilde{W}(t);\tilde{V}_{\beta_1}(t_1),\ldots,\tilde{V}_{\beta_n}(t_n)\rangle\rangle \equiv W_{t;t_1\cdots t_n}^{\beta_1\cdots\beta_n}$. 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.2. Substituting eq B.1 into eq B.4 and comparing the result to eq B.5 yields the wavefunction responses.

$$\tilde{\Psi}_{t;t_1\cdots t_n}^{\beta_1\cdots\beta_n} = (-i)^n\theta(t-t_1)\cdots\theta(t-t_n)\,\mathcal{T}\{\tilde{V}_{\beta_1}(t_1)\cdots\tilde{V}_{\beta_n}(t_n)\}\Psi_0 \tag{B.6}$$

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

$$\langle\langle\tilde{W}(t);\tilde{V}_{\beta_1}(t_1),\ldots,\tilde{V}_{\beta_n}(t_n)\rangle\rangle = \sum_{p=0}^n \frac{1}{p!(n-p)!}\sum_\pi^{\mathrm{S}_n}\langle\tilde{\Psi}_{t;t_{\pi(1)}\cdots t_{\pi(p)}}^{\beta_{\pi(1)}\cdots\beta_{\pi(p)}}|\tilde{W}(t)|\tilde{\Psi}_{t;t_{\pi(p+1)}\cdots t_{\pi(n)}}^{\beta_{\pi(p+1)}\cdots\beta_{\pi(n)}}\rangle \tag{B.7}$$

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

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

Proof: This follows from equations B.6 and B.7 with $n=1$.

Corollary B.1. ***Linear response function (spectral resolution).*** *The linear response function can be expressed as*

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

where $\omega_k \equiv E_k - E_0$ is the excitation energy of the k^{th} stationary state, $H\Psi_k = E_k\Psi_k$.

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

$$\langle\langle\tilde{W}(t);\tilde{V}_\beta(t')\rangle\rangle = -i\theta(t-t')(\langle\Psi_0|We^{-i(H-E_0)(t-t')}V_\beta|\Psi_0\rangle - \langle\Psi_0|V_\beta e^{-i(H-E_0)(t'-t)}W|\Psi_0\rangle) \tag{B.8}$$

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.

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

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

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

Remark C.2. 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.3. $\int_{\mathbb{R}^n} dt_1 \cdots dt_n\, f_{\beta_1}(t_1) \cdots f_{\beta_n}(t_n)\, X^{\beta_1\cdots\beta_n}_{t;t_1\cdots t_n} = \int_{\mathbb{R}^n} d\omega_1 \cdots d\omega_n\, f_{\beta_1}(\omega_{\epsilon,1}) \cdots f_{\beta_n}(\omega_{\epsilon,n}) X^{\beta_1\cdots\beta_n}_{\omega_{\epsilon,1}\cdots\omega_{\epsilon,n}} e^{-i\sum_j \omega_{\epsilon,j} t}$

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

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

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

D Complex Calculus