Take two: Electronic absorption spectrum for a system of two electronic states with one "intramolecular vibration" and a 1D bath via v-FVB/GB incorporating a time-dependent external field.

19Oct15

CINA

From my 17Aug15 notes (and many other places), The Dirac-Frenkel-McLachlan error minimizing condition determining the best $|\dot{\Psi}\rangle$ for any given $|\Psi\rangle$ is

$$0 = \mathrm{Re}\,\langle\delta\dot{\Psi}|\,[H(t)|\Psi\rangle - i|\dot{\Psi}\rangle]\ .$$

If $|\Psi\rangle$ specified by N real parameters λ_n, then

$$|\dot{\Psi}\rangle = \sum_n |\frac{\partial\Psi}{\partial\lambda_n}\rangle\dot{\lambda}_n \equiv \sum_n |\Psi_n\rangle\dot{\lambda}_n\ ,$$

and the Dirac-Frenkel-McLachlan condition can be written more explicitly as

$$0 = \sum_m \delta\dot{\lambda}_n\,\mathrm{Re}\,\langle\Psi_m|[H(t)|\Psi\rangle - i\sum_n|\Psi_n\rangle\dot{\lambda}_n]\ ,$$

and, since the parameter-velocity variations are independent, it follows that $\chi = M\dot{\lambda}$, or

$$\boxed{\dot{\lambda} = M^{-1}\chi}\ ,$$

where $\boxed{\chi_m = \mathrm{Re}\langle\Psi_m|H(t)|\Psi\rangle}$ and $\boxed{M_{mn} = -\,\mathrm{Im}\langle\Psi_m|\Psi_n\rangle}$.

all good to here ✓

Let's consider a situation where $H(t) = H + E v(t)$, with $H = |g\rangle \mathcal{H}_g \langle g| + |e\rangle \mathcal{H}_e \langle e|$. We wish to develop a treatment in which the variational solution is further approximated as a power series in the external field-strength:

$$|\Psi\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle E + \cdots \quad .$$

For now, we'll stop with the first-order term.

Since we are working with a parametrically-specified state, its "expansion coefficients" are determined by those of the parameters themselves. To wit

$$\boxed{|\Psi^{(0)}\rangle = |\Psi\rangle\Big|_{\lambda=\lambda^{(0)}}}$$

$$\boxed{|\Psi^{(1)}\rangle = \sum_n |\Psi_n^{(0)}\rangle \lambda_n^{(1)}}, \quad \text{with} \quad |\Psi_n^{(0)}\rangle \equiv \left|\frac{\partial\Psi}{\partial\lambda_n}\right\rangle\Big|_{\lambda=\lambda^{(0)}},$$

etc.,

where

$$\lambda_n = \lambda_n^{(0)} + E\lambda_n^{(1)} + \cdots \quad .$$

We also need an approximation for

$$|\Psi_n\rangle = \left|\frac{\partial\Psi}{\partial\lambda_n}\right\rangle = |\Psi_n^{(0)}\rangle + E|\Psi_n^{(1)}\rangle + \cdots,$$

$$= \left|\frac{\partial\Psi}{\partial\lambda_n}\right\rangle\Big|_{\lambda=\lambda^{(0)}} + E\sum_m \left|\frac{\partial\Psi_n}{\partial\lambda_m}\right\rangle\Big|_{\lambda=\lambda^{(0)}} \lambda_m^{(1)} + \cdots,$$

whence

$$|\Psi_n^{(0)}\rangle = |\Psi_n\rangle\Big|_{\lambda=\lambda^{(0)}} \quad \text{and} \quad \boxed{|\Psi_n^{(1)}\rangle = \sum_m |\Psi_{nm}^{(0)}\rangle \lambda_m^{(1)}}.$$

again

From the parameter equations of motion on p. 1 we then obtain

$$\dot\lambda^{(0)} = (M^{-1})^{(0)}\,\chi^{(0)}$$

$$\boxed{\dot\lambda^{(0)} = (M^{(0)})^{-1}\chi^{(0)}}\quad , \text{ and}$$

$$\dot\lambda^{(1)} = (M^{-1})^{(0)}\,\chi^{(1)} + (M^{-1})^{(1)}\chi^{(0)}$$

$$\boxed{\dot\lambda^{(1)} = (M^{(0)})^{-1}\,\chi^{(1)} + (M^{-1})^{(1)}\chi^{(0)}}\ .$$

Here, $M^{(0)}_{mn} = -\operatorname{Im}\langle\Psi^{(0)}_m|\Psi^{(0)}_n\rangle$

and $\chi^{(0)}_n = \operatorname{Re}\langle\Psi^{(0)}_n|H|\Psi^{(0)}\rangle$.

N.B. The time-dependent term does not appear

The $\dot\lambda^{(1)}$ term needs to be further developed by incorporating a working expression for $(M^{-1})^{(1)}$. We make use of

$$(M^{(0)}+M^{(1)})^{-1} = \tfrac{1}{2}(M^{(0)})^{-1}\left(1+(M^{(0)})^{-1}M^{(1)}\right)^{-1} + \tfrac{1}{2}\left(1+M^{(1)}(M^{(0)})^{-1}\right)^{-1}(M^{(0)})^{-1}$$

$$\cong (M^{(0)})^{-1} - \tfrac{1}{2}(M^{(0)})^{-2}M^{(1)} - \tfrac{1}{2}M^{(1)}(M^{(0)})^{-2}.$$

Hence

$$\boxed{(M^{-1})^{(1)} = -\tfrac{1}{2}(M^{(0)})^{-2}M^{(1)} - \tfrac{1}{2}M^{(1)}(M^{(0)})^{-2}}\ ,$$

with

$$M^{(1)}_{mn} = -\operatorname{Im}\langle\Psi^{(0)}_m|\Psi^{(1)}_n\rangle - \operatorname{Im}\langle\Psi^{(1)}_m|\Psi^{(0)}_n\rangle$$

$$\boxed{M^{(1)}_{mn} = -\sum_{\ell}\lambda^{(1)}_\ell \operatorname{Im}\{\langle\Psi^{(0)}_m|\Psi^{(0)}_{n\ell}\rangle + \langle\Psi^{(0)}_{m\ell}|\Psi^{(0)}_n\rangle\}}\ .$$

see above for $|\Psi^{(1)}_n\rangle$

or, repeats

The final ingredient in $\dot{\lambda}^{(1)}$ is

$$\chi_n^{(1)} = \mathrm{Re}\langle \Psi_n^{(0)} | v(t) | \Psi^{(0)} \rangle + \mathrm{Re}\langle \Psi_n^{(1)} | H | \Psi^{(0)} \rangle + \mathrm{Re}\langle \Psi_n^{(0)} | H | \Psi^{(1)} \rangle$$

$$\boxed{\chi_n^{(1)} = \mathrm{Re}\langle \Psi_n^{(0)} | v(t) | \Psi^{(0)} \rangle + \sum_k \lambda_k^{(1)} \mathrm{Re}\left\{ \langle \Psi_{nk}^{(0)} | H | \Psi^{(0)} \rangle + \langle \Psi_n^{(0)} | H | \Psi_k^{(0)} \rangle \right\}} .$$

repeats

As a first exercise, we take

$$\mathcal{H}_g = h_g + h_b + v_g \quad \text{and} \quad \mathcal{H}_e = h_e + h_b + v_e ,$$

with $h_{g(e)} = \frac{p^2}{2} + u_{g(e)}(q)$, $h_b = \frac{P^2}{2} + u_b(Q)$,

and $v_{g(e)} = v_{g(e)}(q, Q)$ [v_g has no bilinear (qQ) term, beginning with q^2Q and qQ^2, but v_e might] .

The external interaction takes the form of a single ultrashort pulse centered at time zero:

$$v(t) = -\hat{\mu} f(t) \cos(\Omega t + \varphi) ,$$

with $\hat{\mu} = \mu(|e\rangle\langle g| + |g\rangle\langle e|)$

and $f(t) = \begin{cases} \cos \frac{\pi t}{2\sigma} & -\sigma \le t \le \sigma \\ 0 & \text{otherwise} \end{cases}$.

The ground- and excited-state system Hamiltons have eigenstates and eigenenergies obeying

$$h_{g(e)} | \nu_{g(e)} \rangle = \epsilon_{\nu_{g(e)}} | \nu_{g(e)} \rangle .$$

An arbitrary time-dependent state of the system-plus-bath can be written

$$|\Psi\rangle = |g\rangle \sum_{\nu_g} |\nu_g\rangle |\psi_{\nu_g}\rangle + |e\rangle \sum_{\nu_e} |\nu_e\rangle |\psi_{\nu_e}\rangle ,$$

and, under our FVB/GB ansatz, the bath wave packet accompanying a given system vibronic state is assigned the form

$$\begin{aligned} \langle Q|\psi_{\nu_{g(e)}}\rangle &= a_{\nu_{g(e)}} w_{\nu_{g(e)}}(Q) \\ &= a_{\nu_{g(e)}} e^{\alpha_{\nu_{g(e)}} Q^2 + \beta_{\nu_{g(e)}} Q + i\gamma_{\nu_{g(e)}}} , \end{aligned}$$

where $a_{\nu_{g(e)}}$ and $\gamma_{\nu_{g(e)}}$ are real, time-dependent parameters, $\alpha_{\nu_{g(e)}} = \alpha'_{\nu_{g(e)}} + i\alpha''_{\nu_{g(e)}}$ and $\beta_{\nu_{g(e)}} = \beta'_{\nu_{g(e)}} + i\beta''_{\nu_{g(e)}}$.

The system eigenstates are known, we wish to avoid a presumption that the same is true for the bath, despite the fact that in the present case, the eigenstates of the (1D) bath could be found just as easily as those of the system. As we shall do in general, though, we here assume that the initial state of the system + bath (at some time t_0, before the turn-on of the light pulse) is the overall ground state

$$|\Psi(t_0)\rangle = |g\rangle |0_g\rangle |0_b\rangle e^{-i\epsilon_0 t_0} .$$

Absent a bilinear term in $U_g(q,Q)$ and with neglect of higher-order couplings in the lowest-lying state, $|\Psi(t_0)\rangle$ has been written as a system-bath tensor product. We make the further assumption that cubic and higher-order terms in $u_b(Q)$ do not significantly affect the ground-state of the bath, and hence that it conforms to our Gaussian ansatz; at time t_0, then, we take

$$\boxed{\langle Q|\Psi_{0_g}\rangle = \langle Q|0_b\rangle e^{-i\epsilon_0 t_0} \cong \sqrt[4]{\frac{\omega_b}{\pi}}\, e^{-\frac{\omega_b}{2}Q^2 - i\epsilon_0 t_0}, \text{ with } \epsilon_0 = \epsilon_{0_g} + \frac{\omega_b}{2}},$$

with $\omega_b \equiv \left.\sqrt{\frac{d^2 u_b}{dQ^2}}\right|_{Q=0}$. So the initial values of the bath wave-packet parameters are

$$a_{0_g} = \sqrt[4]{\frac{\omega_b}{\pi}}, \quad \alpha'_{0_g} = -\frac{\omega_b}{2}, \quad \alpha''_{0_g} = 0, \quad \beta'_{0_g} = \beta''_{0_g} = 0,$$

and $\gamma'_{0_g} = -\epsilon_0 t_0$; all a_{ν_e} and $a_{\nu_g \neq 0_g}$ are initially zero.

We set out to calculate the "absorption spectrum" of our system + bath from the spectrally filtered transmission of an ultrashort laserpulse (rather than the simpler strategy of evaluating the Fourier transform of the Heller absorption kernel) in order to try out the perturbative, variational FVB/GB theory. Electronic absorption at frequency $\bar{\omega}$ with resolution $\delta\omega$ can be determined as the loss of electromagnetic energy within a narrow spectral range $\delta\omega$ of $\bar{\omega}$:

$$-\Delta U(\bar{\omega}) = -\frac{1}{4\pi}\int d^3R \left\{ \left[E'(\underset{\sim}{R},t) + \mathcal{E}'(\underset{\sim}{R},t)\right]^2 - E'^2(\underset{\sim}{R},t) \right\}$$

$$\cong -\frac{1}{2\pi}\int d^3R \; E'(\underline{R},t)\,\mathcal{E}'(\underline{R},t)$$

$$= -\frac{1}{2\pi}\int d^3R \; E'(\underset{\sim}{R},t)\,\mathcal{E}(\underline{R},t),$$

where the primes denote spectral filtration.

$$\mathcal{E}(\underline{R},t) = -\frac{1}{c^2R}\,\ddot{\mu}\left(t - \frac{R}{c}\right),$$

where, through first order in E, $\mu = E\mu^{(1)}$, where

$$\mu^{(1)}(t) = \langle \Psi^{(1)} | \hat{\mu} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \hat{\mu} | \Psi^{(1)} \rangle .$$

$$\text{Now, } \quad |\Psi^{(1)}\rangle = |e\rangle \sum_{\nu_e} |\nu_e\rangle |\psi^{(1)}_{\nu_e}\rangle$$

$$= |e\rangle \sum_{\nu_e} |\nu_e\rangle |\psi^{(0)}_{\nu_e\, a_{\nu_e}}\rangle\, a^{(1)}_{\nu_e}$$

$$= |e\rangle \sum_{\nu} |\nu_e\rangle |W^{(0)}_{\nu_e}\rangle\, a^{(1)}_{\nu_e} ,$$

because $|\psi^{(0)}_{\nu_e \lambda}\rangle$ for $\lambda = \alpha'_{\nu_e}, \alpha''_{\nu_e}, \beta'_{\nu_e}, \beta''_{\nu_e}$ and γ_{ν_e} all vanish (e.g., $\langle Q|\psi^{(0)}_{\nu_e \alpha'_{\nu_e}}\rangle = \langle Q|\frac{\partial \psi_{\nu_e}}{\partial \alpha'_{\nu_e}}\rangle\Big|_{E=0}$

$$= a_{\nu_e}\, w_{\nu_e}(Q)\Big|_{E=0} = 0\Big).^{*}$$

Thus,

$$\boxed{\mu^{(1)}(t) = \mu \sum_{\nu_e} \langle \nu_e|0_g\rangle\, a^{(1)}_{\nu_e}\, a^{(0)}_{0_g}\, \langle w_{\nu_e}|w^{(0)}_{0_g}\rangle + \text{c.c.}},$$

in which

$$a^{(0)}_{0_g}\,|w^{(0)}_{0_g}\rangle = |0_b\rangle\, e^{-i\epsilon_0 t}.$$

$$\sqrt[4]{\frac{\omega_b}{\pi}} \qquad \langle Q|w^{(0)}_{0_g}\rangle = e^{-\frac{\omega_b}{2}Q^2} \qquad \epsilon_{0_g} + \frac{\omega_b}{2}$$

$$\langle w^{(0)}_{\nu_e}|w^{(0)}_{0_g}\rangle = \int dQ\, e^{\alpha Q^2 + \beta Q + i\gamma}$$

$$= e^{i\gamma}\, e^{-\frac{\beta^2}{4\alpha}} \sqrt{\frac{\pi}{-\alpha}},$$

with $\gamma = -\epsilon_0 t - \gamma^{(0)}_{\nu_e}$, $\beta = \beta'^{(0)}_{\nu_e} - i\beta''^{(0)}_{\nu_e}$, and $\alpha = \alpha^{(0)}_{\nu_e} - \frac{\omega_b}{2}$.

---

* It is apposite to comment on a possibly confusing issue anent the e-state path wave packets. The parameters defining the various $\langle Q|w_{\nu_e}\rangle$ are undefined (and also irrelevant) initially (i.e., at time t_0), as the corresponding a_{ν_e} are all zero. This fact does not imply that the zero-field limits of $\alpha'_{\nu_e}, \alpha''_{\nu_e}, \beta'_{\nu_e}, \beta''_{\nu_e}$, and γ_{ν_e} vanish for all time. Rather, $\alpha'^{(0)}_{\nu_e}, \ldots, \gamma^{(0)}_{\nu_e}$, have definite values determined by the pulse shape and subsequent evolution

in the e-state specifying the form of the bath wave packet in the limit of vanishing amplitude $a^{(1)}_{\nu e} \to 0$ resulting from vanishingly small electric field strength $E \to 0$.

We next convert the 3D spatial integral for the absorption spectrum, $-\Delta U(\bar{\omega})$, given on p. 7 to a 1D integral over time. The variable t in that expression obeys $t\,\delta\omega \gg 1$ so that the filtered pulse, confined to a slab

$$c\left(t - \tfrac{1}{2}\tfrac{2\pi}{\delta\omega}\right) \lesssim Z \lesssim c\left(t + \tfrac{1}{2}\tfrac{2\pi}{\delta\omega}\right),$$

is well past the molecule located at the origin. It follows that $Z > c\,\frac{2\pi}{\delta\omega} \gg c\,\frac{2\pi}{\omega_0}$ everywhere within this slab, and the spectrally filtered pulse dwells entirely in the molecule's far-zone, which justifies our use of $\mathcal{E} = -\ddot{\mu}/c^2 R$ for the irradiated dipolar field.

Now

$$E'(\underset{\sim}{R},t) = E'(\underset{\sim}{0}, t - Z/c) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega(t - Z/c)}\, \tilde{E}'(\underset{\sim}{0},\omega),$$

so

$$-\Delta U(\bar{\omega}) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega)\, \frac{1}{2\pi c^2} \int_0^{\infty} R\,dR \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\varphi$$

$$\times\, e^{-i\omega(t - \frac{R}{c}\cos\theta)}\, \underbrace{\ddot{\mu}(t - R/c)}$$

$$\boxed{\frac{d^2}{dt^2}\mu(t - R/c) = c^2 \frac{d^2}{dR^2}\mu\left(t - \frac{R}{c}\right)}$$

(continued)

$$-\Delta U(\bar{\omega}) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega)\, e^{-i\omega t} \int_0^\infty R\,dR \int_0^\pi \sin\theta\, d\theta \times e^{i\frac{\omega}{c}R\cos\theta}\, \frac{d^2}{dR^2} u\left(t-\frac{R}{c}\right)$$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega)\, e^{-i\omega t} \int_0^\infty R\,dR \left(-\frac{c}{i\omega R}\right)\left(e^{-i\frac{\omega}{c}R} - e^{i\frac{\omega}{c}R}\right) \frac{d^2}{dR^2} u\left(t-\frac{R}{c}\right)$$

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega) \left(\frac{1}{\omega}\right) e^{-i\omega\left(t+\frac{R}{c}\right)}$$ references

The electric-field strength of the filtered pulse near $z = -R$, which vanishes at time t, so

$$-\Delta U(\bar{\omega}) = \frac{c}{i} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega)\, \frac{1}{\omega} \int_0^\infty dR\, e^{-i\omega\left(t-\frac{R}{c}\right)}\, \frac{d^2}{dR^2} u\left(t-\frac{R}{c}\right)$$

$$= -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega)\, \frac{1}{\omega} \int_{-\infty}^{t} \underbrace{dt'\, e^{-i\omega t'} \frac{d^2}{dt'^2} u(t')}_{\frac{d}{dt'}\left\{e^{-i\omega t'}\frac{d}{dt'}u(t')\right\} + i\omega\, e^{-i\omega t'}\frac{d}{dt'}u(t')}$$

$t' = t - \frac{R}{c}$

gives no contrib'n because filtered probe has no amplitude at the spatial origin at time t or time $-\infty$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \tilde{E}'(\underset{\sim}{0},\omega) \int_{-\infty}^{t} \underbrace{dt'\, e^{-i\omega t'} \frac{d}{dt'} u(t')}_{\underbrace{\frac{d}{dt'}\left\{e^{-i\omega t'} u(t')\right\}}_{\text{no contrib'n}} + i\omega\, e^{-i\omega t'} u(t')}$$

$$= i \int_{-\infty}^{t} dt'\, u(t') \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t'}\, \omega\, \tilde{E}'(\underset{\sim}{0},\omega)$$

The upper limit of t'-integration can be extended to plus infinity because there is no filtered-pulse electric field amplitude at the origin for times later than t. Hence, the absorption spectrum becomes

$$\boxed{-\Delta U(\bar{\omega}) = -\int_{-\infty}^{\infty} dt\, \dot{E}'(\underset{\sim}{0}, t)\, \mu(t)}\ .$$

Using this formula, we need calculate <u>only</u> <u>once</u> the induced dipole (whose first-order term is given on page 8); the absorption at different frequencies is obtained by convolving $\mu(t) \cong E\mu^{(1)}(t)$ with different filtered fields.