Computational methods in molecular quantum dynamics
Discussion 2

Taylor James Baird
taylor.baird@epfl.ch

September 2020

The starting point for our discussion is the time-dependent Schrodinger equation for the general Hamiltonian, $\hat{H}$, describing the dynamics of nuclei and electrons within a molecule. In particular, we may write

$$\hat{H} = \underbrace{\sum_{i=1}^{N} \frac{\hat{p}_i^2}{2M_i}}_{\hat{K}_N} + \underbrace{\sum_{\alpha=1}^{n} \frac{\hat{p}_\alpha^2}{2m} + \frac{1}{2}\sum_i \sum_j \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\hat{R}_i - \hat{R}_j|} - \frac{1}{2}\sum_i \sum_\alpha \frac{Z_i e^2}{4\pi\epsilon_0 |\hat{R}_i - \hat{r}_\alpha|} + \frac{1}{2}\sum_\alpha \sum_\beta \frac{e^2}{4\pi\epsilon_0 |\hat{r}_\alpha - \hat{r}_\beta|}}_{\hat{h}_{el}} \quad (1)$$

$$= \quad \hat{K}_N \quad + \quad \hat{K}_e \quad + \quad \hat{V}_{NN} \quad + \quad \hat{V}_{eN} \quad + \quad \hat{V}_{ee} \quad (2)$$

where n indicates the number of electrons and N indicates the number of nuclei. It is helpful to factor this Hamiltonian, as indicated above, into an electronic Hamiltonian $\hat{h}_{el}$ and a nuclear kinetic energy part $\hat{K}_N$.

And so we want to solve

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \quad (3)$$

Motivated by the observation that the nuclei are much heavier than the electrons, let us consider the limiting case where the nuclei are in fact stationary (clamped nuclei regime).

This leads us to consider an orthonormal basis for the state of our system (called the adiabatic basis) in which the electronic states and the nuclear states are decoupled and can be represented as the following:

$$\{|R\phi_\alpha(R)\rangle\} \quad (4)$$

. where $|\phi_\alpha(R)\rangle$ is an eigenstate of the electronic Hamiltonian:

$$\hat{h}_{el}(\hat{p}, \hat{r}, \hat{R}) |\phi_\alpha(R)\rangle = E_\alpha |\phi_\alpha(R)\rangle \qquad \alpha = 0, \ldots, n_{es} - 1 \quad (5)$$

with $n_e s$ the number of electronic states. R denotes the spatial positions of the nuclei. Note that R denotes ALL the nuclear positions within the system. In the limit of completely stationary nuclei, the dependence of the electronic states on R becomes a **parametric** dependence - consequence of $\hat{h}_{el}$ containing the R-dependent terms $\hat{V}_{eN}$ and $\hat{V}_{NN}$. *Technical note*: Rigorously-speaking, the basis vectors are tensor product states and we should write

$$|R\rangle \otimes |\phi_\alpha(R)\rangle \tag{6}$$

which emphasizes the decoupling (factorization) of the full molecular system's state into an electronic part and a nuclear part. These states live in the tensor product space $\mathcal{H}_N \otimes \mathcal{H}_{el}$ of the electronic Hilbert space and the nuclear Hilbert space.

In this basis, we can expand an arbitrary state vector as

$$|\Psi\rangle = \sum_\alpha \int dR c_\alpha(R) \, |R\phi_\alpha(R)\rangle \tag{7}$$

We use the adiabatic basis to move from the abstract form of the time-dependent Schrodinger equation to its representation w.r.t a specifc set of reference states. Substituing our expansion for $|\Psi\rangle$, we obtain

$$i\hbar\frac{\partial}{\partial t}\sum_\alpha \int dR c_\alpha(R) \, |R\phi_\alpha(R)\rangle = (\hat{K}_N + \hat{h}_{el}) \sum_\alpha \int dR c_\alpha(R) \, |R\phi_\alpha(R)\rangle \tag{8}$$

We wish to see how specific components,$c_\alpha(R)$, of the basis expansion evolve in time. To pick out an individual component, we use the usual trick of projecting onto a specific basis vector $\left|R'\phi_\beta\right\rangle$ and taking advantage of the orthonormality of the basis states. Doing this, we arrive at

$$i\hbar\sum_\alpha \int dR \frac{\partial}{\partial t} c_\alpha(R,t) \, \langle R'\phi_\beta(R')|R\phi_\alpha(R)\rangle = \tag{9}$$

$$\sum_\alpha \int dR c_\alpha(R,t) \left\langle R'\phi_{\beta(R')}\middle|\hat{K}_{N\,el}\middle|R\phi_\alpha(R)\right\rangle \tag{10}$$

$$+\sum_\alpha \int dR c_\alpha(R,t) \, \langle R'\phi_\beta(R')|\hat{h}_{el}|R\phi_\alpha(R)\rangle \tag{11}$$

Consider first the LHS: the basis elements are time-independent and therefore, it becomes

$$i\hbar\sum_\alpha \int dR \delta_{\alpha\beta}\delta(R-R')\frac{\partial}{\partial t}c_\alpha(R,t) \tag{12}$$

and this simplifies to

$$i\hbar\frac{\partial}{\partial t}c_\beta(R',t) \tag{13}$$

Recall that the orthonormality relation for a hybrid continuous-discrete basis takes the form - for two basis vectors $\langle \alpha_1 \mathbf{R} | \alpha_1 \mathbf{R} \rangle$ and $\alpha_2 \mathbf{R}'$ -

$$\langle \alpha_1 \mathbf{R} | \alpha_2 \mathbf{R}' \rangle = \delta_{\alpha_1 \alpha_2} \delta(\mathbf{R} - \mathbf{R}') \tag{14}$$

We have a Dirac delta for the continuous index and a Kronecker delta for the discrete index.

Consider now the second of the terms on the RHS of the TDSE:

$$\sum_\alpha \int dR c_\alpha(R,t) \langle R' \phi_\beta(R') | \hat{h}_{el} | R \phi_\alpha(R) \rangle \tag{15}$$

To proceed with the evaluation of this term, recall the definition of $|\phi_\alpha(R)\rangle$ as the electronic eigenstates of $\hat{h}_{el}$:

$$\hat{h}_{el} |\phi_\alpha(R)\rangle = E_\alpha(R) |\phi_\alpha(R)\rangle \tag{16}$$

.

This allows us to write (15) as

$$\sum_\alpha \int dR E_\alpha(R) c_\alpha(R,t) \langle R' \phi_\beta(R') || R \phi_\alpha(R) \rangle \tag{17}$$

and once again employing the orthonormality condition, this leaves us with

$$\sum_\alpha \int dR E_\alpha(R) c_\alpha(R,t) \delta_{\alpha\beta} \delta(R - R') \tag{18}$$

$$= E_\beta(R') c_\beta(R', t) \tag{19}$$

The final term on the RHS of the Schrodinger equation is the matrix element involving the nuclear kinetic energy operator:

$$\sum_\alpha \int dR c_\alpha(R,t) \left\langle R' \phi_{\beta(R')} \middle| \hat{K}_N \middle| R \phi_\alpha(R) \right\rangle \tag{20}$$

To proceed with its evaluation, let us first recall that the action of the operator $\frac{1}{2M} \hat{p}_i^2$ in the position basis gives rise to the equality

$$\langle R' | \frac{\hat{p}^2}{2M} | R \rangle = -\frac{1}{2M} \frac{\partial^2}{\partial R'^2} \delta(R - R') = -\frac{1}{2M} \frac{\partial^2}{\partial R^2} \delta(R' - R) \tag{21}$$

A quick re-derivation of this identity:

$$\langle R' | \hat{K}_N | R \rangle = \langle R' | \frac{\hat{p}^2}{2M} | R \rangle \tag{22}$$

$$= \frac{1}{2M}\int dp \left\langle R'|p\right\rangle \left\langle p|\hat{p^2}/2M|R\right\rangle \tag{23}$$

$$= \frac{1}{2M}\int dp \frac{e^{iR'p/\hbar}}{\sqrt{2\pi\hbar}} p^2 e^{-iRp/\hbar} \tag{24}$$

$$= \frac{1}{2M}\left(\frac{1}{i\hbar}\right)^2 \frac{\partial^2}{\partial R'^2}\delta(R'-R) = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}\delta(R'-R) \tag{25}$$

Making use of this identity, we have

$$\sum_\alpha \int dR c_\alpha(R,t) \left\langle R'\phi_\beta(R')|\hat{K}_N|R\phi_\alpha(R)\right\rangle \tag{26}$$

$$= -\frac{\hbar^2}{2M}\sum_\alpha \int dR c_\alpha(R,t) \left\langle \phi_\beta(R')|\phi_\alpha(R)\right\rangle \frac{\partial^2}{\partial R^2}\delta(R'-R) \tag{27}$$

Now, we wish to move the partial derivative operator off the Dirac delta function in order to get somewhere with this expression. To do so, remember the usual technique for dealing with such quantities: we simply integrate by parts as many times as necessary before we are left with a delta function on its own (no derivatives acting on it). A quick reminder:

$$\int dx' \frac{\partial}{\partial x}(\delta(x-x'))\psi(x') \tag{28}$$

$$= [\delta(x-x')\psi(x')]\Big|_{-\infty}^{\infty} - \int \delta(x-x')\frac{\partial}{\partial x'}\psi(x') \tag{29}$$

and because wavefunctions (to be physically well-behaved) *must vanish at the boundaries* at $\pm\infty$ this gives

$$-\int dx'\delta(x-x')\frac{\partial}{\partial x'}\psi(x') = -\frac{\partial}{\partial x}\psi(x). \tag{30}$$

So, two applications of the integration by parts formula will let us deal with $\frac{\partial^2}{\partial R^2}\delta(R'-R)$ and leave us with

$$= -\frac{\hbar^2}{2M}\sum_\alpha \int dR \frac{\partial^2}{\partial R^2}(c_\alpha(R,t) \left\langle \phi_\beta(R')|\phi_\alpha(R)\right\rangle)\delta(R'-R) \tag{31}$$

We then have to make use of the product rule for differentiation to expand the 2nd derivative term. This yields:

$$= -\frac{\hbar^2}{2M}\sum_\alpha \int dR\{\frac{\partial^2 c_\alpha(R,t)}{\partial R^2} \left\langle \phi_\beta(R')|\phi_\alpha(R)\right\rangle \tag{32}$$

$$+2\frac{\partial c_\alpha(R,t)}{\partial R}\frac{\partial \left\langle \phi_\beta(R')|\phi_\alpha(R)\right\rangle}{\partial R} + c_\alpha(R,t)\frac{\partial^2 \left\langle \phi_\beta(R')|\phi_\alpha(R)\right\rangle}{\partial R^2}\}\delta(R'-R) \tag{33}$$

. We next use orthonormality of the basis kets (that is $\langle\phi_\beta(R')|\phi_\alpha(R)\rangle = \delta_{\alpha\beta}$) along with the sifting property of the delta function to obtain

$$
\begin{aligned}
&= -\frac{\hbar^2}{2M}\frac{\partial^2 c_\beta(R,t)}{\partial R^2} &(34)\\
&- \frac{\hbar^2}{M}\sum_\alpha \frac{\partial c_\alpha(R,t)}{\partial R}\left\langle \phi_\beta(R) \middle| \frac{\mathrm{d}}{\mathrm{d}R}\phi_\alpha(R)\right\rangle &(35)\\
&- \frac{\hbar^2}{2M}\sum_\alpha c_\alpha(R,t)\left\langle \phi_\beta(R) \middle| \frac{\mathrm{d}^2}{\mathrm{d}R^2}\phi_\alpha(R)\right\rangle &(36)\\
& &(37)
\end{aligned}
$$

Putting everything together, we can finally write the time-dependent Schrodinger equation in the adiabatic basis as:

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}c_\beta(R,t) &= -\frac{\hbar^2}{2M}\frac{\partial^2 c_\beta(R,t)}{\partial R^2} &(38)\\
&- \frac{\hbar^2}{M}\sum_\alpha \frac{\partial c_\alpha(R,t)}{\partial R}\left\langle \phi_\beta(R) \middle| \frac{\mathrm{d}}{\mathrm{d}R}\phi_\alpha(R)\right\rangle &(39)\\
&- \frac{\hbar^2}{2M}\sum_\alpha c_\alpha(R,t)\left\langle \phi_\beta(R) \middle| \frac{\mathrm{d}^2}{\mathrm{d}R^2}\phi_\alpha(R)\right\rangle &(40)\\
&+ E_\beta(R)c_\beta(R,t) &(41)
\end{aligned}
$$