

# Computational Quantum Dynamics — Supplementary Notes

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## 1 Tensor product (clean version)

We make the ansatz for a wave function

$$\Psi(x, y) = \sum_{mn} \sum_{kl} f_k^{(m)}(x) f_l^{(n)}(y) c_{kl}^{(mn)},$$

where the  $f_i^{(m)}(x)$  are suitable finite element functions. Assume a Hamiltonian

$$H = -\frac{1}{2}\partial_x^2 - \frac{1}{2}\partial_y^2 + V(x, y).$$

Continuity conditions must be imposed at the transition between neighboring elements in the form

$$c_{K,j}^{(m,n)} \stackrel{!}{=} c_{0,j}^{(m+1,n)}$$

for each  $i$  occuring on the element  $n$  and

$$c_{i,L}^{(m,n)} \stackrel{!}{=} c_{i,0}^{(m,n+1)}.$$

This can be no longer cast into a simple, block-banded matrix. Rather, the resulting matrix will be a sparse matrix with complicated pattern of zeroes. At this point, it is more convenient to work without explicit identification of neighboring coefficients, but rather impose the conditions as linear constraints in the form

$$\vec{c} \cdot \vec{a}^{(m)} = \vec{c} \cdot \vec{b}^{(n)} = 0.$$

No futher explanation is given here, how this very useful approach works in practice.

For computing matrix elements, we distinguish kinetic and potential energy. Kinetic energy has the natural tensor product form

$$-\Delta = -\partial_x^2 \otimes \mathbf{1} + \mathbf{1} \otimes -\partial_y^2.$$

After discretization in our product basis (on agiven  $m, n$ -patch)

$$|k, l\rangle = |k\rangle \otimes |l\rangle := f_k^{(m)}(x) f_l^{(n)}(y)$$

we have the natural tensor product form

$$\langle k, l | -\Delta | k', l' \rangle =: \widehat{T}_{kl,k'l'} = \left( \widehat{T}^{(x)} \otimes \widehat{S} + \widehat{S} \otimes \widehat{T}^{(y)} \right)_{kl,k'l'},$$

with  $\widehat{T}_{kk'} = \langle k | -\partial_x^2 | k' \rangle$  and  $\widehat{S}_{kk'} = \langle k | k' \rangle$ . This can be very efficiently applied to the coefficients  $c^{(mn)}$  belonging to the given patch.

For the potential, we use a different strategy. We try to find quadrature grid points and weights on each coordinate

$$(q_i^{(x)}, q_j^{(y)}), (w_i^{(x)}, w_j^{(y)}),$$

such the integrals are well approximated (we drop the patch indices  $m, n$ )

$$\int dx dy f_k(x) f_l(y) V(x, y) f'_k(x) f'_l(y) \approx \sum_{i,j} f_k(q_i^{(x)}) f_l(q_j^{(y)}) w_i^{(x)} w_j^{(y)} V(q_i^{(x)}, q_j^{(y)}) f'_k(q_i^{(x)}) f'_l(q_j^{(y)}).$$

Defining the matrices (assuming for simplicity  $q_i^{(x)} = q_i^{(y)} =: q_i$ )

$$F_{ik} := f_k(q_i)$$

and the diagonal matrix

$$V(q_i, q_j) =: \delta_{ii'} \delta_{jj'} V_{ij, i'j'},$$

we see that applying potential to a coefficient vector take the shape

$$\sum_{i'j'} \langle ij | V | i'j' \rangle c_{i'j'} = \left[ \left( \widehat{F}^T \otimes \widehat{F}^T \right) \widehat{V} \left( \widehat{F} \otimes \widehat{F} \right) \vec{c} \right]_{ij}$$

i.e. a sequence of tensor-product — diagonal matrix — tensor product, which brings down the operations count dramatically, if the dimension of the the factor spaces are not too small, larger than 4. The operations count for both factor spaces dimension  $N$  and number of grid points  $K$  is

$$\underbrace{2NK^2}_{\text{second tensor}} + \underbrace{K^2}_{\text{diagonal}} + \underbrace{2KN^2}_{\text{first tensor}}$$

Compare that to the operations count  $N^4$  of applying the full operator directly. Note that  $K \gtrsim N$ .

## 2 Molecules

If one could keep the nuclei in fixed positions, the electronic structure of molecules can be described, in principle, by the same techniques as for atoms. The lower symmetry of molecules (they are never invariant under general rotations), further increases the technical difficulties and, except for the simple case of the  $H_2^+$  ion, the only way to obtain reasonable descriptions of the electronic structure of molecules is by numerical methods. There are well developed quantum chemistry computer codes available for this task, some of them are free (e.g. GAMESS).

### 2.1 The Born-Oppenheimer ansatz

In reality, the nuclei are not fixed. The motion of the nuclei changes the relative positions of the attractive Coulomb centers and with it changes the electronic structure. But at least, at the available energies, the nuclei move much slower than the electrons: the ratio of the even the lightest nucleus (proton) mass to the electron mass is 2000:1. Classically speaking, we may assume that the electron moves many times through its orbit before a noticeable change of the nuclear position occurs. To study the nuclear motion in the field of the electron, we can just as well average over the electronic motion. This is the justification to separate the dynamics of the electron from that of the nuclei. Averaging over the classical electronic motion here would correspond to assume the electron remains in a quantum mechanical eigenstate.

Let us look at the simplest possible diatomic molecule, more precisely the molecular ion  $H_2^+$ , which consists of two nuclei of charge  $Z = 1$  and one electron. We use the coordinates  $\vec{R}$  and  $\vec{r}$ . The Hamiltonian is

$$\begin{aligned} H &= -\frac{1}{2}\Delta_r - \frac{1}{|\vec{r} - \vec{R}/2|} - \frac{1}{|\vec{r} + \vec{R}/2|} - \frac{1}{M}\Delta_R + \frac{1}{R} \\ &= H_e(\vec{R}) - \frac{1}{M}\Delta_R = H_e + T_n \end{aligned}$$

where  $M$  is the reduced mass of the relative nuclear motion  $M = m_p^2/2m_p = m_p/2$  for the proton mass  $m_p$ . We have indicated a separation into “electronic” part  $H_e(\vec{R})$  at fixed nuclear position  $\vec{R}$  and the kinetic energy of relative nuclear motion  $T_n$ .

The idea of the Born-Oppenheimer approximation is to compute the ground state energy  $E(\vec{R})$  of the electron at fixed nuclear positions  $\vec{R}$ . In our simple example this energy will not depend on the direction of  $\vec{R}$  but only on the internuclear distance  $R$ . As the total energy is constant, when the nuclei change position they need to convert some of their kinetic energy to compensate for the change in electron (ground state) energy: the electron energy  $E(R)$  acts as a potential for the nuclear motion. This potential is called the **Born-Oppenheimer potential**. We can now study the (quantum mechanical) motion of the nuclei in that potential.

Thus we arrive at the basic Born-Oppenheimer method.

- Find  $E(R)$ , the lowest energy eigenvalue of  $H_e$

$$H_e(R)\Phi(R, \vec{r}) = E(R)\Phi(R, \vec{r})$$

for all  $R$  (in practice: for sufficiently many different  $R$ 's).

- Solve the Schrödinger equation for the nuclear motion in the potential  $E(R)$ . As in our simple case the potential is rotationally symmetric, it is enough to solve the radial Schrödinger equation for the angular momenta  $J$

$$\left[ -\frac{1}{2M} \frac{1}{R} \partial_R^2 R + \frac{J(J+1)}{2MR^2} + E(R) \right] \chi_{\nu J}(R) = E_{\nu J} \chi_{\nu J}(R)$$

We find the ground and excited energies of *nuclear* motion  $E_{00}$  and  $E_{\nu J}$ .  $\nu$  refers to the relative motion of the nuclei is called the “vibrational quantum number”,  $J$  the rotational q.n.

The approximate wave function of the complete system is

$$\Psi(\vec{r}, \vec{R}) \approx Y_{JM}(\hat{R}) \chi_{\nu J}(R) \Phi(R, \vec{r}).$$

Clearly, this is not an exact eigenfunction.

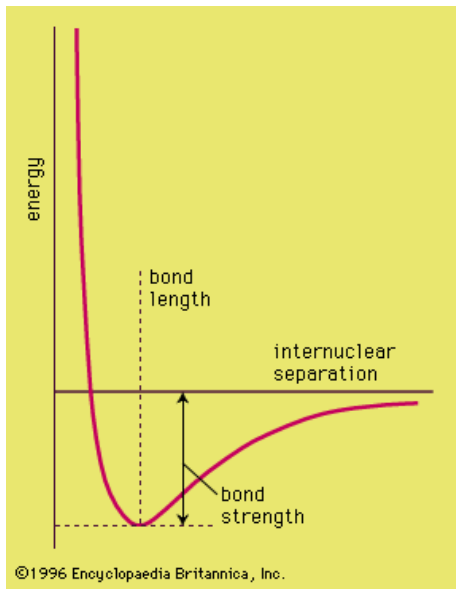


Figure 1: Typical shape of a Born-Oppenheimer potential corresponding to the electronic ground state. The separation of the nuclei will be approximately where the potential has its minimum. The nuclei cannot approach each other closely, because of their Coulomb repulsion, potential  $Z_1 Z_2 / R$ . At large distances the potential becomes flat, binding forces weaken and the molecule can dissociate.

**Problem 2.1:** The error of the Born-Oppenheimer wave function compared to exact solutions can be calculated by inserting

$$\Psi_{BO}(\vec{r}, \vec{R}) = Y_{JM}(\hat{R}) \chi_{\nu J}(R) \Phi(R, \vec{r})$$

into the Schrödinger equation. Do this for the simplest case  $J = 0$  and show that the error is

$$\sim -\frac{2}{MR} [\partial_R R \chi(R)] [\partial_R \Phi(R, \vec{r})] - \frac{1}{M} [\chi(R)] [\partial_R^2 \Phi(R, \vec{r})].$$

We see that the error is related to how rapidly  $\Phi(R, \vec{r})$  changes with  $R$  and it is proportional to  $1/M$ . If  $M$  is large enough and no dramatic things happen in the derivatives  $\partial_R \Phi(R, \vec{r})$ , the error of the Born-Oppenheimer approximation becomes small. If for some reason  $\Phi(R, \vec{r})$  changes rapidly with  $R$ , the approximation breaks down. This does indeed occur, as we discuss below.

## 2.2 Potential energy curves and avoided crossing

But why should the electron be in its ground state? Actually, it does not need to be. The BO scheme can be readily generalized to include excited electronic states.

The extension goes as follows

- Find  $E_i(R)$ , the eigenvalues of electronic part of the Hamiltonian

$$H_e(R) \Phi_i(R, \vec{r}) = E_i(R) \Phi_i(R, \vec{r})$$

for all  $R$ .

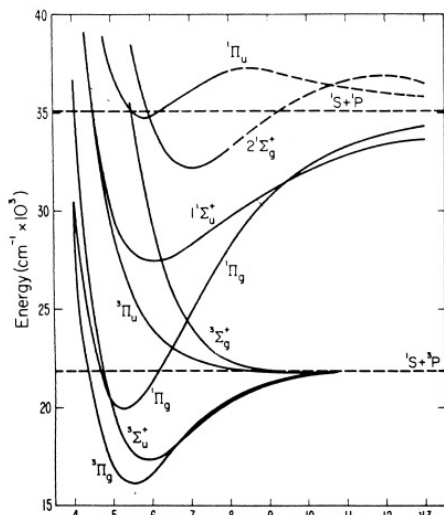
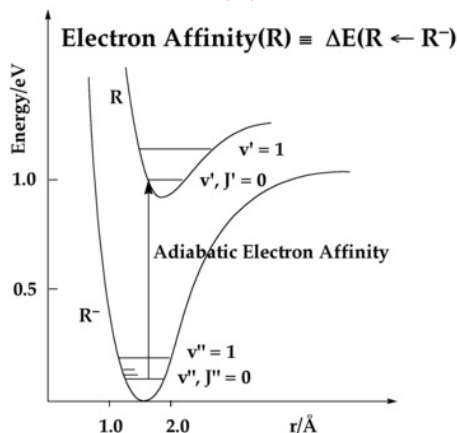
- Solve the Schrödinger equation for the nuclear motion for each potential  $E_i(R)$ .

$$\left[ -\frac{1}{2M} \frac{1}{R} \partial_R^2 R + \frac{J(J+1)}{2MR^2} + E_i(R) \right] \chi_{\nu}^{(i)}(R) = E_{\nu J}^{(i)} \chi_{\nu}^{(i)}(R)$$

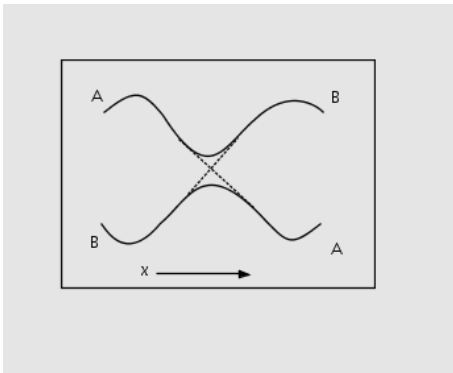
We now have different nuclear eigenstates  $\chi_{\nu}^{(i)}(R)$  for different “**potential energy curves**”  $E_i(R)$ . Approximate eigenfunctions for given electronic excitation  $i$  and vibrational and rotational quantum numbers  $\nu, J$  are

$$\Psi_{\nu, J}^{(i)}(\vec{r}, \vec{R}) \approx Y_{JM}(\hat{R}) \chi_{\nu J}^{(i)}(R) \Phi_i(R, \vec{r}).$$

Note that  $i$  does not refer to one electronic state, but to all states that sit different values of  $R$  with their respective energies  $E_i(R)$ : it is a whole *curve* of potential energies.



It can happen that for some value of  $R$  two subsequent electronic energies  $E_i(R)$  and  $E_{i+1}(R)$  get close to each other. There is a general theorem that for the diatomic case the energies can never exactly coincide, the curves can never cross. They can only cross if they belong to parts the electronic Hamiltonian that are independent due to symmetry, think of electronic wave functions with different angular momenta or parity. One speaks of “**avoided crossings**”. Exactly near those avoided crossings the BO approximation breaks down, as the electronic wave functions change rapidly with  $R$ .



We do not attempt to demonstrate this behavior here directly. Rather, use a different way of seeing this is by looking at the characteristic time scales: the whole BO approximation is based on the idea that the nuclei move slowly, but the electrons move quickly. The characteristic time scale for electronic motion is given by the energy differences between electronic states. Think of two energies  $E_1$  and  $E_2$ , then a superposition of the two corresponding states leads to a “beat” in electron density at the period  $T = 2\pi/|E_1 - E_2|$ :

A superposition state formed by two energy eigenstates  $\Phi_1$  and  $\Phi_2$  with energies  $E_1$  and  $E_2$ , has the

time-evolution

$$\Psi(t) = e^{-iE_1 t} \Phi_1 + e^{-iE_2 t} \Phi_2$$

and the electron density

$$|\Psi(t, \vec{x})|^2 = |\Phi_1(\vec{x})|^2 + |\Phi_2(\vec{x})|^2 + 2 \cos[(E_1 - E_2)t] \Re e \Phi_1^*(\vec{x}) \Phi_2(\vec{x})$$

When the difference between some  $E_i$  and  $E_{i+1}$  becomes comparable to the difference between the vibrational  $E_{\nu+1J} - E_{\nu J}$  or rotational  $E_{\nu J+1} - E_{\nu J}$  energies of the nuclei, the electronic motion cannot be separated from the nuclear motion and the assumption for the BO approximation is violated.

The situation can be repaired with moderate effort, by solving for a combined wave packed on both potential energy curves simultaneously and also taking into account the coupling between the surfaces near the avoided crossings.

## 2.3 Franck-Condon transitions

Suppose the nuclei are in their lowest state  $|\chi_{00}^{(0)}\rangle$  within the lowest potential energy curve  $E_0(R)$ , that is the system is in its ground state. Now a photon is absorbed and changes the the electronic system from  $E_0$  to  $E_1$ . This is assumed to happen suddenly compared to the time scale of the nuclear motion. The wave function  $\chi_{00}^{(0)}(R)$  finds itself in a new potential  $E_1(R)$ , where it is not an eigenstate. However, it can be expanded into the eigenstates  $|\chi_{\nu J}^{(1)}\rangle$  for the potential energy curve  $E_1$

$$|\chi_{00}^{(0)}\rangle = \sum_{\nu, J} |\chi_{\nu J}^{(1)}\rangle \langle \chi_{\nu J}^{(1)} | \chi_{00}^{(0)} \rangle$$

This type of an excitation is call a **“Franck-Condon transition”** with the Franck-Condon factors  $\langle \chi_{\nu J}^{(1)} | \chi_{00}^{(0)} \rangle$ . The probability for a photon to be absorbed will also depend on how large the Franck-Condon factors for the transition are for the differences in the joint electronic and nuclear energies corresponding to the photon.

### 2.3.1 Multi-atomic molecules, potential surfaces

The Born-Oppenheimer approximation is not restricted to diatomic molecules. On the contrary, the approach is the the central tool for describing chemical reactions of all kinds in often very complex molecules. The generalized procedure is

- For a system with  $n_e$  electrons and  $N$  nuclei define a electronic Hamiltonian by

$$H_e(\vec{R}_1, \dots, \vec{R}_N) = H - \sum_{i=1}^N T_i$$

where  $T_i$  is the kinetic energy term  $-\Delta_{R_i}/(2M_i)$  of the  $i$ th nucleus.

- Find  $E(\vec{R}_1, \dots, \vec{R}_N)$ , the ground state energy of  $H_e$

$$H_e(\vec{R}_1, \dots, \vec{R}_N) \Phi(\vec{R}_1, \dots, \vec{R}_N; \vec{r}) = E(\vec{R}_1, \dots, \vec{R}_N) \Phi(R, \vec{r})$$

on a sufficiently large number of grid points in the multi-dimensional space of nuclear coordinates.  $E(\vec{R}_1, \dots, \vec{R}_N)$  is a very high-dimensional surface.

- Solve the Schrödinger equation for the nuclear motion on the potential energy surface

$$\left[ \sum_{i=1}^N T_i + E(\vec{R}_1, \dots, \vec{R}_N) \right] \chi(\vec{R}_1, \dots, \vec{R}_N) = E \chi(\vec{R}_1, \dots, \vec{R}_N)$$

This all means very large scale computations, but it is feasible. It can also be extended to excited states stacking several potential energy surfaces on top of each other.

Note that, different from one-dimensional potential energy curves, potential energy surfaces can cross. These crossings turn out to play a key role many photo-chemical reactions. I.e. reactions where light is absorbed and causes structural changes in the molecule.

### 3 Topics (preliminary)

Each topic should be presented by a team of 2-3 people. The presentation includes the mathematical / theoretical background, the general structure of provided code and possibly of newly written code, demonstration of the usage, proof of correctness, and numerical examples (convergence, accuracy). Where applicable, also physical interpretation and representation of data.

Using the TDSEsolver: wave-packet propagation in one dimension
Linear algebra in C++: eigen, lapack, storage formats
Visualization
Finite elements at work: accuracy, stability, etc.
Numerical integration by Gauss quadrature: Legendre, Laguerre, Gauss, general
Finding the ground state: propagation in imaginary time, Arnoldi method
ODE solvers — a numerical comparison
Wave packed dynamics: femtochemistry, dynamics on potential energy surfaces
Field-ionization of atoms and molecules
Multipole operators: spherical harmonics, Clebsch-Gordan coefficients
Absorption: exterior complex scaling vs. complex absorbing potentials
Two-electron systems: 3d Helium atom in inter-particle coordinates, $L = 0$ and $L > 0$
Helium: in 1d, direct discretization time-dependent
Helium: in 1d, Hartree-Fock, time-dependent Hartree-Fock

#### 3.1 Born-Oppenheimer dynamics

Use the 2 x 1d model system

$$H(x, y) = -\frac{1}{2}\partial_x^2 - V_a(x - y/2) - V_a(x + y/2) - \frac{1}{2M}\partial_y^2 + V_b(y)$$

where  $x$  and  $y$  play the roles of “electronic” and “nuclear” coordinates, respectively. Use the “screened Coulomb” model potential

$$V_c(x) = \frac{1}{\sqrt{x^2 + c}}$$

Leave  $a$  and  $b$  as input parameters, but default values of  $a = b = 2$  are a good choice. Similarly, the nuclear mass is an input parameter, but an obvious choice is  $M = 1000$  (in units of the electron mass), which is the reduced mass of proton relative motion.

Your tasks:

- Solve the electronic eigenvalue problem, get BO potentials for ground and first few excited states; for that, create your own, new `discretization` class, modifying `simple`.
- Create a class to do BO for multiple surfaces. Feed the numerically determined  $V_{BO}^{(n)}$  into that (may read from file, use C++ `cinp`, examples can be found in the code).
- Compute the vibrational spectrum of in BO approximation (i.e. the  $E_\nu$ ), compare this spectrum to the exact one, using the 2x1d Helium code of the preceding seminar.
- Use your colleagues “wave packet dynamics” code study wave-packet time-evolution on the first excited BO surface (check Frank-Condon transition in the attached notes on BO).