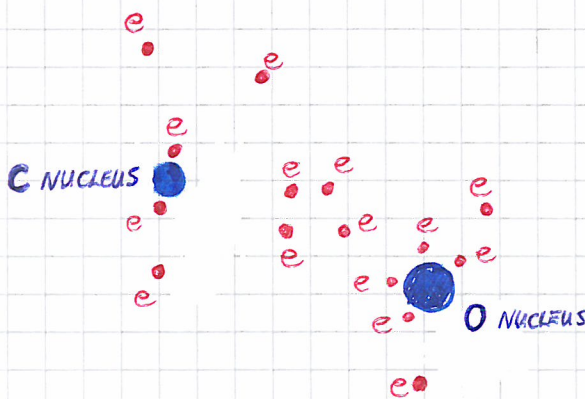


2. BORN-OPPENHEIMER APPROXIMATION

The oldest formulation of an adiabatic approximation in QM was actually given only a couple of years after QM was discovered, by Born & Oppenheimer in 1927. It is useful even now to recall their argument, which was given in a wave-function formulation, and to then rephrase the argument in a more modern form. The modern formulation makes it clear how the separation of energy scales is made, and it leads itself to a systematic adiabatic expansion.

2(a) ORIGINAL FORMULATION: The question asked by Born & Oppenheimer was originally couched in atomic physics terms; the problem was to solve for nuclear dynamics in a molecule, in the presence of rapidly moving electrons, and at the same time to find the electronic dynamics.



Consider, eg., the situation shown at left, which is supposed to be a snapshot of an instantaneous configuration of a CO molecule.

There are 2 slowly moving nuclei, of mass $\sim 29,000$ electron masses (for the O nucleus), and $\sim 20,000$ electron masses (for the C nucleus). Thus quite clearly the electrons move so quickly in comparison to the nuclei

that we can, to first approximation, treat the nuclei as stationary. The Born-Oppenheimer approximation is the next approximation beyond this.

We begin by considering a more general problem. Suppose we have a slow system, with coordinate Q and canonical momentum P , and it is

coupled to a set of fast-moving variables $X = (x_1, \dots, x_N)$. There is an interaction between them, and so we write the Hamiltonian as

FAST VARIABLES \times

$V(Q, X)$

SLOW VARIABLES Q

$$\mathcal{H}(Q, X; \Lambda) = \mathcal{H}_0(Q; \Lambda) + \mathcal{H}_e(X, \Lambda) + V(Q, X; \Lambda) \quad (1)$$

where Λ is an ultraviolet cutoff, which must be specified if the Hamiltonian is to be

well-defined. Later on we will explore more fully the role of this cutoff, whose value can be varied.

Now the Born-Oppenheimer trick, in its original form, was to write down the following ansatz for the total wave-function for the system, as follows: We define the "adiabatic eigenstates" $|\varphi_n(Q, x)\rangle$ of the fast Hamiltonian, as

$$[\mathcal{H}_E^0(x) + V(\varphi, x)] |\varphi_n(Q, x)\rangle = E_n(\varphi) |\varphi_n(Q, x)\rangle \quad (2)$$

Note that this is a standard monovariate - compare eqn (32) in section (1) of this discussion of slow PM. We now write the solution to the full Hamiltonian, viz.

$$\mathcal{H} |\Psi(\varphi, x)\rangle = E |\Psi(\varphi, x)\rangle \quad (3)$$

in the form (ignoring time-dependence):
$$|\Psi(\varphi, x)\rangle = \sum_n \Phi_n(\varphi) |\varphi_n(\varphi, x)\rangle \quad (4)$$

so that the $\Phi_n(\varphi)$ act as the coefficients in the expansion of Ψ . If we put the time-dependence in explicitly, we have

$$\Psi(\varphi(t); x(t)) = \sum_n \Phi_n(\varphi(t); t) \varphi_n(\varphi(t), x(t)) e^{-\frac{i}{\hbar} \int dt' E_n(\varphi(t'))} \quad (5)$$

which should be compared with eqn (33) in section (1).

However we recognize from looking at (4) that not only can we view the coefficients $\Phi_n(\varphi)$ as the expansion coefficients for the fast variable wave-functions $\varphi_n(\varphi, x)$ (in analogy with the $C_n(g(x))$ in section (1)); we can also think of them as the adiabatic wave-functions of the slow variables. Let's pursue this, by substituting (4) into (3). We then have

$$\sum_n [\mathcal{H}_0(\varphi) + V(\varphi, x) + \mathcal{H}_E^0(x)] \Phi_n(\varphi) |\varphi_n(\varphi, x)\rangle = E \sum_n \Phi_n(\varphi) |\varphi_n(\varphi, x)\rangle \quad (6)$$

and in the usual way we now multiply on the left by $\langle \varphi_m(\varphi, x) |$ and take the inner product, to get

$$\sum_n \langle \varphi_m | \mathcal{H}_0(\varphi) \Phi_n(\varphi) | \varphi_n \rangle + E_m(\varphi) \Phi_m(\varphi) = E \Phi_m(\varphi) \quad (7)$$

This is now an equation for the slow wave-function $\Phi_m(\varphi)$. To proceed further it is useful to give an explicit form for the slow variable Hamiltonian $\mathcal{H}_0(\varphi)$. We will assume that

$$\mathcal{H}_0(\varphi) = \frac{P^2}{2M_0} + \mathcal{U}(\varphi) = \left[-\frac{\hbar^2}{2M_0} \nabla_\varphi^2 + \mathcal{U}(\varphi) \right] \quad (8)$$

It is now a matter of simple manipulation to show that the eqn. (7) can be written as

$$\mathcal{H}_{\alpha\beta}^{\text{eff}}(\varphi) \Phi_{\beta}(\varphi) = E \Phi_{\alpha}(\varphi) \quad (9)$$

where the effective Hamiltonian $\mathcal{H}^{\text{eff}}(\varphi)$ has matrix elements

$$\begin{aligned} \mathcal{H}_{\alpha\beta}^{\text{eff}}(\varphi) &\equiv \langle \varphi_{\alpha} | \mathcal{H}^{\text{eff}}(\varphi) | \varphi_{\beta} \rangle \\ &= \left\{ \frac{-\hbar^2}{2M_0} \sum_{\gamma} \left[(\delta_{\alpha\gamma} \nabla_{\varphi} - i \underline{A}_{\alpha\gamma}(\varphi)) (\delta_{\gamma\beta} \nabla_{\varphi} - i \underline{A}_{\gamma\beta}(\varphi)) \right] \right. \\ &\quad \left. + \delta_{\alpha\beta} [\epsilon_{\alpha}(\varphi) + \mathcal{U}(\varphi)] \right\} \end{aligned} \quad (10)$$

and where we have defined the (non-Abelian) gauge potential:

$$\underline{A}_{\alpha\beta}(\varphi) = i \langle \varphi_{\alpha} | \nabla_{\varphi} | \varphi_{\beta} \rangle \quad (11)$$

Now the final Born-Oppenheimer approximation keeps only the diagonal matrix elements of this gauge potential, i.e., it ignores transitions between the different fast levels that might be mediated by the motion of the slow variables. One then writes:

$$\mathcal{H}_{\alpha}^{\text{BO}} = \frac{-\hbar^2}{2M_0} (\nabla_{\varphi} - i \underline{A}_{\alpha}(\varphi))^2 + \mathcal{U}_{\alpha}^{\text{eff}}(\varphi) \quad (12)$$

with
$$\mathcal{U}_{\alpha}^{\text{eff}}(\varphi) = [\epsilon_{\alpha}(\varphi) + \mathcal{U}(\varphi)] \quad (13)$$

$$\underline{A}_{\alpha}(\varphi) = i \delta_{\alpha\beta} \langle \varphi_{\alpha} | \nabla_{\varphi} | \varphi_{\alpha} \rangle \quad (14)$$

Notice that to get $\mathcal{H}^{\text{eff}}(\varphi)$ in the form (10), we have expanded out the matrix elements in (7):

$$\langle \varphi_{\alpha} | \nabla_{\varphi}^2 (\Phi_{\beta} | \varphi_{\beta} \rangle) = \sum_{\gamma} (\delta_{\alpha\gamma} \nabla_{\varphi} - i \underline{A}_{\alpha\gamma}(\varphi)) (\delta_{\gamma\beta} \nabla_{\varphi} - i \underline{A}_{\gamma\beta}(\varphi)) \Phi_{\beta} \quad (15)$$

The similarity of this development to that in the discussion of the adiabatic regime in QM, given in the last section, is obvious. In the same way as before, we can also write

$$\underline{A}_{\alpha\beta}(\varphi) = i \frac{\langle \varphi_{\alpha} | \nabla_{\varphi} \mathcal{H} | \varphi_{\beta} \rangle}{\epsilon_{\alpha}(\varphi) - \epsilon_{\beta}(\varphi)} \quad (16)$$

and all of the previous discussion given of the physics of such gauge potentials, in section (1), can be done here. Thus one can define a field

$$\begin{aligned}
 \underline{B}_\alpha(\underline{Q}) &= \nabla_{\underline{Q}} \times \underline{A}_\alpha(\underline{Q}) = g_m [\nabla_{\underline{Q}} \times \langle \varphi_\alpha | \nabla_{\underline{Q}} \varphi_\alpha(\underline{Q}) \rangle] \\
 &= g_m [\langle \nabla_{\underline{Q}} \varphi_\alpha(\underline{Q}) | \times | \nabla_{\underline{Q}} \varphi_\alpha(\underline{Q}) \rangle]
 \end{aligned}
 \tag{17}$$

which can also be written as

$$\underline{B}_\alpha(\underline{Q}) = g_m \sum_{\beta \neq \alpha} \frac{\langle \varphi_\alpha(\underline{Q}) | \nabla_{\underline{Q}} \mathcal{H} | \varphi_\beta(\underline{Q}) \rangle \times \langle \varphi_\beta(\underline{Q}) | \nabla_{\underline{Q}} \mathcal{H} | \varphi_\alpha(\underline{Q}) \rangle}{(\epsilon_\alpha(\underline{Q}) - \epsilon_\beta(\underline{Q}))^2}
 \tag{18}$$

and if we now imagine taking the slow system round a circuit in \underline{Q} -space, we get a phase factor

$$\gamma_\alpha(\mathcal{C}) = \oint d\underline{Q} \cdot \underline{A}_\alpha(\underline{Q})
 \tag{19}$$

in the wave-function $\Phi_\alpha(\underline{Q})$, which is just a Berry phase.

We will pursue the connection between these results and the results given in section (1) below. However it is first interesting and intuitively useful to recall how chemists & physical chemists have understood these results in the past (long before Berry phases, etc.). In the chemistry literature, the following correspondence is made:

$$\begin{aligned}
 \underline{Q} &\rightarrow \underline{R}_j \quad (\text{coordinates of } j\text{-th nucleus}) \\
 \underline{X} &\rightarrow (\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \quad (\text{coordinates of the } N \text{ electrons}) \\
 \epsilon_n(\underline{Q}) &\rightarrow \epsilon_n(\underline{R}_j) \quad (\text{electronic energy levels, for a specific set of nuclear positions}) \\
 \mathcal{U}_{\text{eff}}^\alpha(\underline{Q}) &\rightarrow \mathcal{U}_{\text{eff}}^\alpha(\underline{R}_j) \quad (\text{Effective potential for nuclear motion in presence of electrons in state } |\varphi_\alpha\rangle)
 \end{aligned}
 \tag{20}$$

and also

$$\underline{A}_\alpha(\underline{Q}) \rightarrow \underline{A}_\alpha(\underline{R}_j)
 \tag{21}$$

Before the 1990's, the attention of practically-minded chemists focussed on the quantities in (20), even though it was actually chemists (beginning with Longuet-Higgins & Herzberg in 1963) who first focussed attention on these

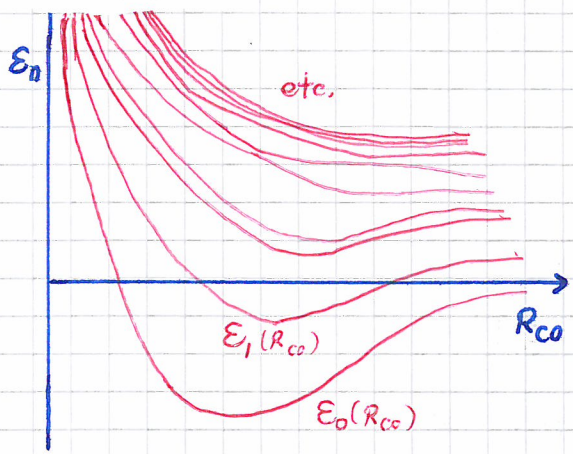
extra phase factors - essentially all of the above results were already derived by the theoretical chemists Møller & Tushler in 1949.

In most of the physical chemistry literature, the following intuitive ideas are used:

(a) One has a set of electronic levels $E_n(\underline{R}_J)$, with wave-functions

$$\langle \sum_k \delta(\underline{r}_k - \underline{r}_k) | \varphi_n(\underline{R}_J) \rangle = \varphi_n(\underline{R}_J, \underline{r}_k) \quad (22)$$

which depend on the nuclear coordinates \underline{R}_J , but where, in the Born-Oppenheimer approximation, one ignores all transitions between these levels - it is assumed, at least for the lowest electronic levels, that the level splitting $E_{n+1}(\underline{R}) - E_n(\underline{R})$ is always quite large, so that the quantity



can to first approximation be neglected.

$$A_{n+1,n} = i \langle \varphi_{n+1} | \nabla_R | \varphi_n \rangle \quad (23)$$

To give an idea of how this works, we consider again the CO molecule. Clearly the electronic levels of this molecule do not depend on the orientation of the vector $\underline{R}_{CO} = \underline{R}_C - \underline{R}_O$, nor on the centre of mass coordinate $R_{com} = \frac{1}{2}(\underline{R}_C + \underline{R}_O)$, if the 2 atoms are isolated in free space. The only dependence will be on $R_{CO} = |\underline{R}_C - \underline{R}_O|$, and the expected behaviour is shown above - note that this result is derived in molecular physics by solving the following Hamiltonian

$$\hat{H}_e |\varphi_n\rangle = E_n |\varphi_n\rangle \quad (24)$$

$$\left. \begin{aligned} \hat{H}_e &= T_e + V_{ee} + V_{en} \\ &= \sum_{k=1}^N \frac{-\hbar^2}{2m_e} \nabla_k^2 + \frac{1}{2} \sum_{k \neq k'} \frac{e^2}{|\underline{r}_k - \underline{r}_{k'}|} + \sum_{j=1,2} \sum_{k=1}^N \frac{Q_j e^2}{|\underline{R}_j - \underline{r}_k|} \end{aligned} \right\} \quad (25)$$

where \underline{R}_j are the nuclear positions, Q_j the nuclear atomic numbers, e the electronic charge, \underline{r}_k the electronic positions, and $\nabla_k \equiv \partial/\partial \underline{r}_k$. The shape of the curves in the figure is the result of complex electronic screening effects

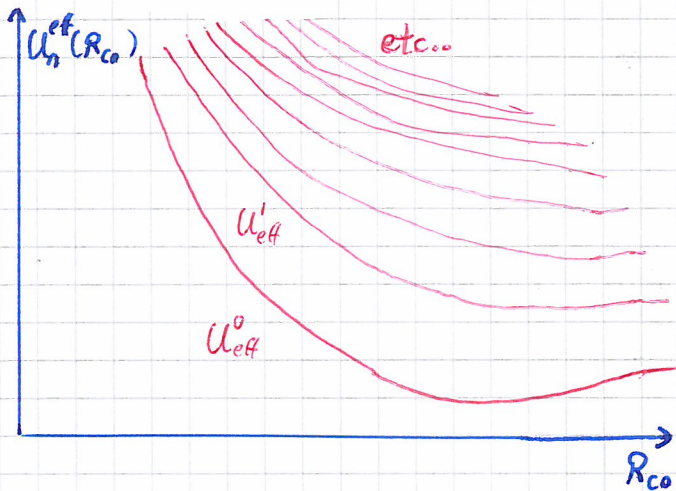
(b) One also has the effective potential acting on the nuclear motion, which for this system is written

$$U_{eff}^n(\underline{R}) = E_n(\underline{R}) + V_{NN}(\underline{R}) \quad (26)$$

where $V_{NN}(\underline{R})$ is simply the internuclear interaction:

$$V_{NN}(\underline{R}) = \sum_{i \neq j} \frac{q_i q_j e^2}{|R_i - R_j|} \quad (27)$$

and so the renormalised interaction $U_{eff}(\underline{R})$ looks similar to the energy levels for the electrons.



Chemists refer to these levels, as a function of the multi-dimensional coordinates $\underline{R} = \{R_j\}$, as "Born-Oppenheimer energy surfaces"; we see that they are nothing but the adiabatic energy levels that we have already met in the previous section. Most information of use to chemists is contained within these energy surfaces - one can use them in

calculations of everything from vibration spectra to chemical reaction rates.

What about the gauge field $A_n(\underline{R})$? It is clear from the above that this variable is connected with rotations of the nuclei around each other. Thus, in the example of CO, we can imagine moving the O around the C in a circuit. Then we see immediately that a Berry phase

$$\begin{aligned} \gamma_n(\mathcal{C}) &= i \oint d\underline{R} \cdot \langle \varphi_n | \nabla_{\underline{R}} | \varphi_n \rangle \\ &\equiv i \oint d\underline{R}_{CO} \cdot \langle \varphi_n(\underline{R}_{CO}) | \nabla_{\underline{R}_{CO}} | \varphi_n(\underline{R}_{CO}) \rangle \end{aligned} \quad (28)$$

will be incorporated into the molecular wave function $\Phi_n(\underline{R}_{CO})$. In this sense the origin, $\underline{R}_{CO} \rightarrow 0$, of the coordinate sets like a "magnetic pole" in the wave-function, adding an extra phase when we move around it.

There is no space to continue this discussion - see the references if you are interested in more details.

Let us now summarize what has been done. The total wave-function for the PAIR of systems has been written in an expansion over the eigenfunctions of the fast system, written as functions of a slowly-varying parameter Φ which refers to the slow system. Analysis of these coefficients $\Phi_m(\Phi)$ of this expansion, which are ADIABATIC WAVE-FUNCTIONS for the slow system, shows they satisfy a standard adiabatic eqn of motion.

2(b) PATH INTEGRAL FORMULATION

The main problem with the original Born-Oppenheimer formulation of their approximation is that there is no obvious way to extend it systematically - one would like to know how the corrections work.

This problem lends itself perfectly to path integral methods, which are not limited by perturbation theory, and which can be set up so as to systematically expand things in some "slowness" parameter.

We assume again the Hamiltonian (1), and define again the eigenstates $|\varphi_n(\varphi)\rangle$ of the "fast" part of the Hamiltonian, as in (2). We accordingly write the Lagrangian in the form

$$\begin{aligned} \mathcal{L}(Q, X) &= L_0(Q) + L_{\text{int}}(Q, X) + L_E(X) \\ &\equiv L_0(Q) + \mathcal{L}^{\text{fast}}(Q, X) \end{aligned} \quad (29)$$

and accordingly we write the propagator for the combined fast + slow variables in the form:

$$\begin{aligned} \mathcal{G}(\varphi_2, x_2; \varphi_1, x_1; t_2, t_1) &= \int_{\varphi_1}^{\varphi_2} \mathcal{D}q(\tau) \int_{x_1}^{x_2} \mathcal{D}x(\tau) e^{i\hbar^{-1} \int_{t_1}^{t_2} \mathcal{L}(q, x)} \\ &= \int_{\varphi_1}^{\varphi_2} \mathcal{D}q(\tau) e^{i\hbar^{-1} \int_{t_1}^{t_2} L_0(q)} \int_{x_1}^{x_2} \mathcal{D}x(\tau) e^{i\hbar^{-1} \int_{t_1}^{t_2} [L_{\text{int}}(q, x) + L_E(x)]} \end{aligned} \quad (30)$$

$$= \int \mathcal{D}q(\tau) e^{i\hbar^{-1} \int_{t_1}^{t_2} L_0(q)} G_F(x_2, x_1; t_2, t_1; [q(\tau)]) \quad (31)$$

Here we have defined a new object, the Green function $G_F(q, t; [q])$, which is a Green function for the fast variables, conditional on a GIVEN PATH $q(\tau)$ of the slow variables.

Consider 2 different ways we might evaluate this fast Green function, depending on which states we use as basis functions:

(a) Suppose we try to calculate G_F by expanding it in the eigenstates of the independent environment. Thus we would first define a Green function

$$\hat{G}_0^E(t) = |\mu\rangle e^{-i\hbar^{-1} \epsilon_\mu^0 t} \langle \mu| \quad (32)$$

where the states $|\mu\rangle$ are eigenstates of \hat{H}_E :

$$\hat{H}_E |\mu\rangle = \epsilon_\mu^0 |\mu\rangle \quad (33)$$

The advantage of this approach is that because $H_E(x)$ is time-independent, we can write everything in terms of the time-independent energies E_μ , and the states $| \mu \rangle$.

The disadvantage is that the Green function $G_f [q(t)]$ may be very hard to calculate, unless the states $| \mu \rangle$ and the Hamiltonian $H_E(x)$ are simple. Thus, eg., the function $G_f [q(t)]$ can be found in closed form if H_E can be written as a set of oscillator "normal modes"; this is the problem solved by Feynman when he first developed path integral theory.

(b) We write G_f by expanding in terms of the eigenstates $| n(q) \rangle$ of the fast Lagrangian $L_{fast} [q]$, with q taken as a parameter. Now, in developments familiar from the discussion of QM in the adiabatic regime, we write the the time evolution of these states as follows:

$$\psi(t) = U^f(t) | n(q(0)) \rangle \tag{34}$$

where the time evolution operator is

$$U^f(t) = \hat{T} e^{-i/\hbar \int dt' H_f(q(t'), t')} \tag{36}$$

Now from the theory of adiabatic processes, we recall that in the adiabatic regime we can write, for an initial state $| n(q(0)) \rangle$, that the subsequent state will be:

$$\psi(t) = \sum_m | m(q(t)) \rangle e^{-i/\hbar \int dt' [E_n(q(t')) \delta_{mn} + i\hbar \dot{q} \cdot \langle m | \nabla_q n(q) \rangle]} \tag{37}$$

where, as in (2), the $E_n(q)$ are the eigenfunctions of the fast part of the Lagrangian:

$$H_f(q, x) | n(q) \rangle = [H_E(x) + V_{int}(q, x)] | n(q) \rangle = E_n(q) | n(q) \rangle \tag{38}$$

and we note that (37) also follows from the simple identity:

$$\begin{aligned} i\hbar \frac{d}{dt} | n(q(t)) \rangle &= i\hbar [\partial_t | n(q(t)) \rangle + \dot{q} \cdot \nabla_q | n(q(t)) \rangle] \\ &= \sum_m [E_n(q(t)) \delta_{mn} + i\hbar \dot{q} \cdot \langle m(q) | \nabla_q n(q) \rangle] | m(q(t)) \rangle \end{aligned} \tag{39}$$

The form of the fast Green fn. follows immediately from (37):

$$\begin{aligned} \hat{G}^f [q(t)] &= | m \rangle G_{mn}^f [q(t)] \langle n | \equiv | m \rangle \langle m | U^f(t) | n \rangle \langle n | \\ &\rightarrow | m(q(t)) \rangle e^{-i/\hbar \int dt' [E_n(q(t')) \delta_{mn} + i\hbar \dot{q} \cdot \langle m(q) | \nabla_q n(q) \rangle]} \langle n(q(t)) | \end{aligned} \tag{40}$$

Now we incorporate this fast Green function into the total \mathcal{G} ; from (31) and (40) we can write this as

$$\begin{aligned} \mathcal{G}(\varphi_2 \varphi_1; x_2 x_1; t_2 t_1) &= \sum_{mn} \int_{\varphi_1}^{\varphi_2} \mathcal{D}q(\tau) e^{\frac{i}{\hbar} \int d\tau L_0(q)} \langle x_2 | m(q(\tau)) \rangle G_{mn}^f[q] \langle n(q(\tau)) | x_1 \rangle \\ &\equiv \sum_{mn} \int_{\varphi_1}^{\varphi_2} \mathcal{D}q(\tau) \langle x_2 | m \rangle e^{\frac{i}{\hbar} \int d\tau [L_0(q) - \varepsilon_n(q) \delta_{mn} - i\hbar \dot{q} \cdot \langle m | \nabla_q | n \rangle]} \langle n | x_1 \rangle \end{aligned} \quad (41)$$

ie, as an expansion over the adiabatic eigenstates $|n(q(\tau))\rangle$. In effect we have derived an expression of form

$$\begin{aligned} \mathcal{G}(\varphi_2 \varphi_1; x_2 x_1; t_2 t_1) &= \sum_{mn} \langle \varphi_2 x_2 | m \rangle \mathcal{G}_{mn}^{\text{eff}}(t_2 t_1) \langle n | \varphi_1 x_1 \rangle \\ &\equiv \sum_{mn} \langle x_2 | m(\varphi_2) \rangle \mathcal{G}_{mn}^{\text{eff}}(t_2 t_1) \langle n(\varphi_1) | x_1 \rangle \end{aligned} \quad (42)$$

$$\text{where } \mathcal{G}_{mn}^{\text{eff}}(t_2 t_1) = \int_m^n \mathcal{D}q(\tau) e^{\frac{i}{\hbar} \int_{t_1}^{t_2} L_{mn}^{\text{eff}}(q)}$$

$$\text{in which we define the integration measure } \int_m^n \mathcal{D}q(\tau) \equiv \Phi_m^+(\varphi_2) \Phi_n^-(\varphi_1) \int_{\varphi_1}^{\varphi_2} \mathcal{D}q(\tau) \quad (43)$$

and the effective Lagrangian

$$\begin{aligned} L_{mn}^{\text{eff}}(q, \dot{q}, t) &= \{ L_0(q) \delta_{mn} - \varepsilon_n(q) \delta_{mn} - i\hbar \dot{q} \cdot \langle m(q) | \nabla_q | n(q) \rangle \} \\ &= \{ [L_0(q) - \varepsilon_n(q)] \delta_{mn} - i\hbar \dot{q} \cdot A_{mn}(q) \} \end{aligned} \quad (44)$$

with $A_{mn}(q)$ defined as before. The Born-Oppenheimer approximation, in its original form, then just consists in dropping the non-diagonal elements of $L_{\text{eff}}(q)$, to get an effective Lagrangian

$$L_n^{\text{BO}}(\varphi) = L_0^{\text{eff}}(\varphi) - \mathcal{V}_{\text{eff}}^n(\varphi) \quad (45)$$

$$\begin{aligned} \text{where } L_0^{\text{eff}}(\varphi, \dot{\varphi}) &= \frac{1}{2} M \dot{\varphi}^2 - \frac{1}{2} \dot{\varphi} \cdot \underline{A}_n(\varphi) \\ \mathcal{V}_{\text{eff}}^n(\varphi) &= \varepsilon_n(\varphi) + \mathcal{U}(\varphi) \end{aligned} \quad (46)$$

We note that these expressions can be used as the starting point for a renormalisation, in which some fast degrees of freedom are truncated out.