The AC Stark Effect, Time–Dependent Born–Oppenheimer Approximation, and Franck–Condon Factors

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Abstract

We study the quantum mechanics of a simple molecular system that is subject to a laser pulse. We model the laser pulse by a classical oscillatory electric field, and we employ the Born–Oppenheimer approximation for the molecule. We compute transition amplitudes to leading order in the laser strength. These amplitudes contain Franck–Condon factors that we compute explicitly to leading order in the Born–Oppenheimer parameter.

We also correct an erroneous calculation in the mathematical literature on the AC Stark effect for molecular systems.

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1 Introduction

In many experimental situations, laser pulses are used to stimulate electronic transitions in molecules. After such a transition, a molecule is typically in a superposition of many vibrational states for the nuclei. The main goal of this paper is to study these transitions in a simple molecular model, and to calculate the particular superposition of vibrational states.

In the physics literature, problems of this type have a long history, with intuition and formulas that date back to the early days of quantum mechanics. The results rely on two approximations. The first is the Born–Oppenheimer approximation, which separates the nuclear and electronic motions. In this approximation, the electronic bound state energy levels depend on the nuclear positions, and these electronic energy levels play the role of effective potentials for the nuclei. This approximation depends on the smallness of the parameter ϵ, which is the fourth root of the electron mass divided by the mean nuclear mass. The second approximation involves the idea that electronic transitions occur on a time scale that is very short compared with that of the nuclear motion. Often, the term "vertical transition" is used. This terminology comes from plotting the nuclear positions

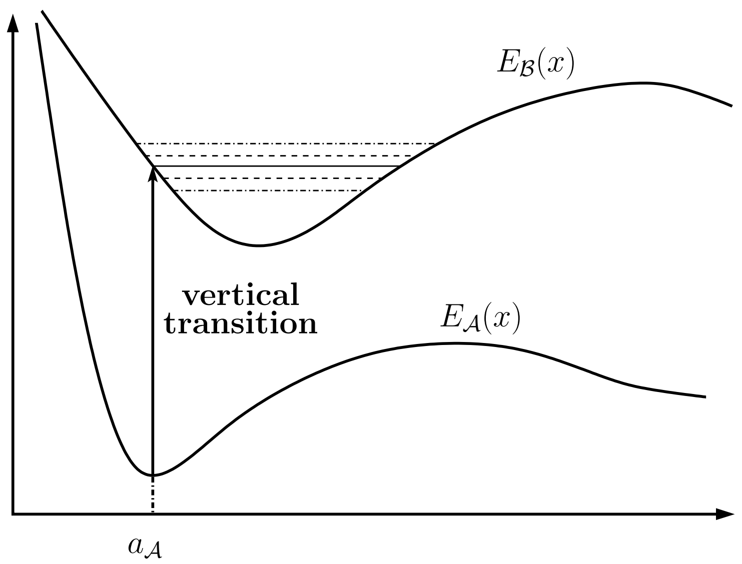

Figure 1: Graphical interpretation of a vertical transition

on a horizontal axis and electron energy levels on the vertical axis, as in Figure 1. If the nuclei do not move during a transition, then a change of electronic state corresponds just to a vertical change on the plot. Quantitatively, this idea corresponds to the nuclear wave packet not changing during the time that the electrons are making the transition.

Although the molecule may start in a single bound state before the electronic transition, it typically is not in a single bound state after the transition because the nuclei find themselves subject to a different effective potential. However, if the nuclei are in a well of the new electron energy level, the final nuclear state can be expanded as a superposition of bound states of the new well. The expansion coefficients are called the Franck–Condon factors [1, 2, 3].

We prove that this intuition is correct to first order in the laser field strength μ, and we present a formula for the Franck–Condon factors to leading order in ϵ. For technical reasons, we do this for a situation where the nuclei have only one degree of freedom. This model is specifically relevant to diatomic molecules where the single degree of freedom is the distance between the nuclei.

In addition, we correct some calculations in [11, 12]. Those articles study the time–dependent Born–Oppenheimer approximation in the presence of a laser pulse. They develop expansions jointly in ϵ and μ for the full molecular wave function. The error we correct stems from the inadvertent commuting of two operators that do not commute (in the middle of a long calculation). The error is largely hidden in the complicated notation that the problem appears to require.

The paper is organized as follows: In Section 2, we make a precise statement of the problem and introduce the notation we require. In Section 3, we study electronic transitions to leading order in ϵ and first order in μ. We prove that the intuition described above is correct, and we present the expression for the Franck–Condon factors the leading order in ϵ. Our main result is summarized in Theorem 3.1. In Section 4, we indicate how to correct the calculational error in [11, 12].

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2 Precise Formulation of the Problem

Our goal is to study approximate solutions to the molecular Schrödinger equation

$$i\,\epsilon^2\,\frac{\partial\Psi}{\partial t} \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2\Psi}{\partial x^2}\,+\,h(x)\,\Psi\,+\,\mu\,X\,f(t,\,\epsilon)\,\Psi. \tag{2.1}$$

for small ϵ and small μ. Here Ψ is a function of the nuclear configuration x, and takes its values in a Hilbert space $\mathcal{H}_{\mathrm{el}}$ that we call the electronic Hilbert space. The operator $h(x)$ is called the electronic Hamiltonian. It is self–adjoint on $\mathcal{H}_{\mathrm{el}}$ and depends smoothly on x in a strong resolvent sense. Discrete eigenvalues of $h(x)$ that depend smoothly on x are called electron energy levels.

We assume $h(x)$ has two non–degenerate eigenvalues $E_{\mathcal{A}}(x)$ and $E_{\mathcal{B}}(x)$ that are each isolated from the rest of the spectrum and from one another. We denote the corresponding normalized electron eigenvectors by $\Phi_{\mathcal{A}}(x)$ and $\Phi_{\mathcal{B}}(x)$. We choose the phases of these eigenvectors so that they each satisfy $\langle\,\Phi(x),\,\Phi'(x)\,\rangle_{\mathcal{H}_{\mathrm{el}}} = 0$. If they can be chosen to be real vectors in some L^2 space, this phase condition is automatically satisfied.

We assume $E_{\mathcal{A}}$ has local minimum at $x = a_{\mathcal{A}}$ with $E''_{\mathcal{A}}(a_{\mathcal{A}}) > 0$. We further assume that $x = a_{\mathcal{A}}$ lies inside a well of $E_{\mathcal{B}}$. We require either that $a_{\mathcal{A}}$ be a local minimum of $E_{\mathcal{B}}$ with $E''_{\mathcal{B}}(a_{\mathcal{A}}) > 0$ or that both $E'_{\mathcal{B}}(a_{\mathcal{A}}) \neq 0$ and that within that well, any local maxima of $E_{\mathcal{B}}$ lie strictly below $E_{\mathcal{B}}(a_{\mathcal{A}})$. So that we are considering bound states instead of resonances, we assume $E_{\mathcal{A}}(a_{\mathcal{A}})$ and $E_{\mathcal{B}}(a_{\mathcal{A}})$ lie strictly below $\liminf\limits_{|x|\to\infty}\,\inf\,\sigma(h(x))$.

For most of our arguments, the specific form of f is not essential. However, to model realistic laser pulses, we can take $f(t,\,\epsilon)$ to have the form

$$f(t,\,\epsilon) \;=\; \epsilon^{-q}\;f_0\left(\,t/\epsilon^{2-q}\,\right)\;\cos\left(\,\omega\,t/\epsilon^2\,\right),$$

with $0 \le q \le 2$. A reasonable choice of f_0 is a non-negative smooth function of compact support that specifies an envelope for the pulse.

For simplicity, we assume that X is a bounded operator on the electron Hilbert space. The more general situation where X may be unbounded and may also act on the nuclei can be handled as in [11, 12]. Because of the large masses of the nuclei as $\epsilon \to 0$, and because the laser field oscillates very rapidly on the time scale of the nuclei, inclusion of the action of X on the nuclei has no effect to leading order in ϵ.

2.1 Born–Oppenheimer Preliminaries

In this section we collect several known results that we need. These concern semiclassical wave packets and both the time–dependent and time–independent Born–Oppenheimer approximations. More detailed discussions of these results can be found in the references we have cited.

2.1.1 Semiclassical Wave Packets

The time–dependent Born–Oppenheimer approximation makes use of certain semiclassical wave packets for the nuclei. In one dimension, these may be written as

$$\begin{aligned} &\phi_m(A, B, \epsilon^2, a, \eta, x) \qquad\qquad (2.2)\\ &\quad = \; 2^{-m/2}\,(m!)^{-1/2}\,\left(\overline{A}/A\right)^{m/2}\; H_m\left(\hbar^{-1/2}|A|^{-1}(x-a)\right)\;\phi_0(A, B, \epsilon^2, a, \eta, x), \end{aligned}$$

where $m = 0,\, 1,\, 2,\, \cdots$, and

$$\phi_0(A, B, \epsilon^2, a, \eta, x) \;=\; \pi^{-1/4}\,\epsilon^{-1/2}\,A^{-1/2}\;\exp\left(\,-\,\frac{B\,(x-a)^2}{2\,A\,\epsilon^2}\;+\;i\;\frac{\eta\,(x-a)}{\epsilon^2}\,\right).$$

We always assume A and B are chosen to satisfy $\mathrm{Re}\,(\overline{B}\,A) \;=\; 1$. Each of these states ϕ_m is concentrated near the classical position a and its (scaled) Fourier transform is concentrated near the classical momentum η. The uncertainty in position is $\epsilon\,\sqrt{m+1/2}\;|A|$ and its uncertainty in momentum is $\epsilon\,\sqrt{m+1/2}\;|B|$. For fixed a, η, A, and B, these functions form an orthonormal basis of $L^2(I\!\!R)$, indexed by m. Numerous properties of these semiclassical wave packets and their higher dimensional analogs are discussed in [9].

2.1.2 Lowlying Vibrational States

We take our initial conditions for (2.1) to be the $m^{\rm th}$ vibrational state associated with the electronic level $E_{\mathcal{A}}$. From known results of the time–independent Born–Oppenheimer approximation [6], this state equals

$$\phi_m(A_{\mathcal{A}}, B_{\mathcal{A}}, \epsilon^2, a_{\mathcal{A}}, 0, x)\, \Phi_{\mathcal{A}}(x) \;+\; O(\epsilon), \tag{2.3}$$

where $A_{\mathcal{A}} = 1/\omega_{\mathcal{A}}$ and $B_{\mathcal{A}} = \omega_{\mathcal{A}}$ with $\omega_{\mathcal{A}} \,=\, \sqrt{E''_{\mathcal{A}}(a_{\mathcal{A}})}$.

The energy of this state is $E_{\mathcal{A},m} \;=\; E_{\mathcal{A}}(a_{\mathcal{A}}) \;+\; \epsilon^2\,(m+1/2)\,\omega_{\mathcal{A}} \;+\; O(\epsilon^4)$.

2.1.3 The Leading Order Time–Dependent Born–Oppenheimer Approximation

Except in Section 4, we only require the leading order time–dependent Born–Oppenheimer approximation [5, 7, 8]. For any given isolated non–degenerate electron level $E_{\mathcal{C}}(x)$ with normalized eigenfunction $\Phi_{\mathcal{C}}(x)$ with $\langle\, \Phi_{\mathcal{C}}(x),\, \Phi'_{\mathcal{C}}(x)\,\rangle_{\mathcal{H}_{\rm el}} = 0$, equation (2.1) with $\mu = 0$ has solutions of the form

$$e^{iS(t)/\epsilon^2}\;\phi_m(A(t), B(t), \epsilon^2, a(t), \eta(t), x)\;\Phi_{\mathcal{C}}(x) \;+\; O(\epsilon), \tag{2.4}$$

where

$$\dot{a}(t) \;=\; \eta(t), \tag{2.5}$$

$$\dot{\eta}(t) \;=\; -\,E'_{\mathcal{C}}(a(t)), \tag{2.6}$$

$$\dot{A}(t) \;=\; i\,B(t), \tag{2.7}$$

$$\dot{B}(t) \;=\; i\,E''_{\mathcal{C}}(a(t))\,A(t), \qquad \text{and} \tag{2.8}$$

$$\dot{S}(t) \;=\; \frac{\eta(t)^2}{2} \;-\; E_{\mathcal{C}}(a(t)). \tag{2.9}$$

We use the symbol $U_{BO}(t,\,s)$ to indicate the lowest order Born–Oppenheimer propagation, which agrees with the exact propagator up to an $O(\epsilon)$ error when applied to any semiclassical wave packet in x times a discrete eigenstate of $h(x)$.

2.1.4 Molecular Bound States Near a Fixed Energy

Although our initial state is the m^{th} vibrational state of the well for $E_{\mathcal{A}}$, the component of the wave function that has made an electronic transition is generically in a superposition of highly excited vibrational states for the well $E_{\mathcal{B}}$. The energy of these excited states is near $E_{\mathcal{B}}(a_{\mathcal{A}})$, but the vibrational levels have energy spacing $O(\epsilon^2)$, so a relevant vibrational level is the n^{th} one, where $n = O(\epsilon^{-2})$. These states are rigorously studied as quasimodes in [13, 14]. The n^{th} quasimode is $\psi_{n,\epsilon}(x)\,\Phi_{\mathcal{B}}(x) + O(\epsilon)$, where $\psi_{n,\epsilon}$ can be written as an integral over a classical trajectory for the potential $E_{\mathcal{B}}$ to leading order in ϵ. To avoid confusion with the time t in our problem, we parameterize the orbit by the time variable r. More precisely,

$$\begin{aligned}
\psi_{n,\epsilon}(x) \quad &= \quad \pi^{-1/4}\,\epsilon^{-1/2}\sqrt{\frac{|\theta|}{2\,\tau(E)}} \qquad\qquad (2.10)\\
&\times \quad \int_{-\tau(E)/2}^{\tau(E)/2} e^{ir\left(E+\frac{\pi\epsilon^2}{\tau(E)}\right)/\epsilon^2}\; e^{iS(r)/\epsilon^2}\;\phi_0(A(r),B(r),\epsilon^2,a(r),\eta(r),x)\;dr \;+\; O(\epsilon).
\end{aligned}$$

Here the orbit's energy E is chosen to satisfy the Bohr–Sommerfeld condition that the classical action $I(E)$ of the orbit of energy E must have $\dfrac{I(E)}{2\pi\epsilon^2}$ equal to a non-negative integer. We note that $I(E)/(2\pi)$ is the area of the region of phase space surrounded by the orbit. We denote the period of the orbit by $\tau(E) = \dfrac{\partial I}{\partial E}(E)$. The energy of the quasimode is $E_{\mathcal{B},n} = E + \dfrac{\pi\epsilon^2}{\tau(E)} + O(\epsilon^3)$. We choose $a(0) = a_0$, $\eta_0 = 0$, $A(0) = A_{\mathcal{A}}$, $B(0) = B_{\mathcal{A}}$, $S(0) = 0$, and $\theta = E_{\mathcal{B}}'(a_0)A_{\mathcal{A}}$, where a_0 is the point near $a_{\mathcal{A}}$ where $E_{\mathcal{B}}(a_0) = E$. The $a(r)$, $\eta(r)$ and $S(r)$ satisfy (2.5), (2.6), and (2.9) with $\mathcal{C} = \mathcal{B}$, and r in place of t. The $A(r)$ and $B(r)$ satisfy

$$\begin{aligned}
\dot{A}(r) \quad &= \quad i\,B(r) \,+\, 2\,\alpha(E)\,\eta(r)\,(E_{\mathcal{B}}'(a(r))A(r) + i\eta(r)B(r)),\\
\dot{B}(r) \quad &= \quad i\,E_{\mathcal{B}}''(a(r))\,A(r) \,+\, 2\,i\,\alpha(E)\,E_{\mathcal{B}}'(a(r))\,(E_{\mathcal{B}}'(a(r))A(r) + i\eta(r)B(r)).
\end{aligned}$$

The quantity $\alpha(E)$ in these equations is $\alpha(E) = \dfrac{\tau'(E)}{2\,\tau(E)}$.

See [10, 13, 14] for detailed discussions.

3 Electronic Transitions and Franck–Condon Factors

Our main result is summarized by the following theorem.

Theorem 3.1 *Let $\Psi(x,\,t,\,\epsilon)$ denote the solution to the Schrödinger equation (2.1) with initial condition*

$$\Psi(x,\,t_0,\,\epsilon) \;=\; \phi_m(A_{\mathcal{A}}, B_{\mathcal{A}}, \epsilon^2, a_{\mathcal{A}}, 0, x)\;\Phi_{\mathcal{A}}(x),$$

where $t_0 \,<\, \inf\,\mathrm{supp}\, f(\,\cdot\,,\,\epsilon)$.

Then for $t \,>\, \sup\,\mathrm{supp}\, f(\,\cdot\,,\,\epsilon)$, *the component of* $\Psi(x,\,t,\,\epsilon)$ *that is a multiple of* $\Phi_{\mathcal{B}}(x)$ *is*

$$\mu\; e^{it_0(E_{\mathcal{A},m})/\epsilon^2}\,\sum_n\, G_\epsilon(n,\,m)\; FC_\epsilon(n,\,m)\; e^{-itE_{\mathcal{B},n}/\epsilon^2}\;\psi_{n,\epsilon}(x)\;\Phi_{\mathcal{B}}(x)\;+\;O(\mu^2)\;+\;O(\mu\,\epsilon),$$

where the Franck–Condon factor is $FC_\epsilon(n,\,m) = \langle\,\psi_{n,\epsilon}(x),\,\phi_m(A_{\mathcal{A}}, B_{\mathcal{A}}, \epsilon^2, a_{\mathcal{A}}, 0, x)\,\rangle$.

In the generic case where $E'_{\mathcal{B}}(a_{\mathcal{A}}) \,\neq\, 0$,

$$\begin{aligned} FC_\epsilon(n,\,m) \;&=\; \frac{\pi^{1/4}\;2^{-(m-1)/2}\;\epsilon^{1/2}}{\sqrt{m!\;\tau(E_{\mathcal{B}}(a_{\mathcal{A}}))\,|E'_{\mathcal{B}}(a_{\mathcal{A}})|\,A_{\mathcal{A}}}}\;H_m\left(\frac{B_{\mathcal{A}}\,\left(E_{\mathcal{B},n}-E_{\mathcal{B}}(a_{\mathcal{A}})-\frac{\pi\epsilon^2}{\tau(E_{\mathcal{B}}(a_{\mathcal{A}}))}\right)}{|E'_{\mathcal{B}}(a_{\mathcal{A}})|\,\epsilon}\right) \\ &\quad\times\;\exp\left(-\,\frac{B_{\mathcal{A}}^2\,\left(E_{\mathcal{B},n}-E_{\mathcal{B}}(a_{\mathcal{A}})-\frac{\pi\epsilon^2}{\tau(E_{\mathcal{B}}(a_{\mathcal{A}}))}\right)^2}{2\,E'_{\mathcal{B}}(a_{\mathcal{A}})^2\,\epsilon^2}\right)\;(\,1\;+\;O(\epsilon^p)\,)\,, \end{aligned} \tag{3.1}$$

where $p > 0$.
In the non-generic case where $E'_{\mathcal{B}}(a_{\mathcal{A}}) = 0$, *we assume* $E''_{\mathcal{B}}(a_{\mathcal{A}}) > 0$.
In this case, if $n-m$ *is odd, then* $FC_\epsilon(n,\,m) = 0$, *and if* $n-m$ *is even, then*

$$\begin{aligned} FC_\epsilon(n,\,m) \;&=\; 2^{-\frac{m+n-1}{2}}\;\left(r+\frac{1}{r}\right)^{-\frac{m+n+1}{2}} \\ &\quad\times\sum_{\substack{j\,=\,0\\ m-j\ \text{even}\\ n-j\ \text{even}}}^{\min(n,m)}\;\frac{(-1)^{\frac{n-j}{2}}\sqrt{(n!)(m!)}\;4^j}{j!}\;\left(r-\frac{1}{r}\right)^{\frac{m+n}{2}-j}\;w(m-j)\;w(n-j), \end{aligned} \tag{3.2}$$

where $r \;=\; \dfrac{\omega_{\mathcal{A}}}{\omega_{\mathcal{B}}}$ *and* $w(p) \;=\; \begin{cases} 1 & \textit{if}\;\; p=0,\\[4pt] \dfrac{2}{p\,((\frac{p}{2}-1)!)} & \textit{if}\;\; p=2,\,4,\,6,\cdots. \end{cases}$

If $f(t,\,\epsilon) \;=\; \epsilon^q\, f_0\,(t/\epsilon^{2-q})\;\cos\,(\omega\, t/\epsilon^2)$ *with* $0 \le q \le 2$, *then*

$$G_\epsilon(n,\,m) \;=\; -\,i\,\sqrt{\frac{\pi}{2}}\;X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\;\left[\;\widehat{f_0}\left(\frac{E_{\mathcal{A},m}-E_{\mathcal{B},n}(\epsilon)+\omega}{\epsilon^q}\right)\right. \qquad (3.3)$$

$$\left. +\;\;\widehat{f_0}\left(\frac{E_{\mathcal{A},m}-E_{\mathcal{B},n}(\epsilon)-\omega}{\epsilon^q}\right)\;\right],$$

where $X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}}) \;=\; \langle\,\Phi_{\mathcal{B}}(a_{\mathcal{A}}),\,X\,\Phi_{\mathcal{A}}(a_{\mathcal{A}})\,\rangle_{\mathcal{H}_{\rm el}}$.

Remarks.

1. In physically realistic situations, the $X_{\mathcal{B}\mathcal{A}}(x)$ is calculated from an electric dipole moment of the molecule.

2. If f_0 is very smooth and $q>0$, then the quantity (3.3) will only be large where the change in energy in the transition is $\pm\,\omega$. This corresponds intuitively to the absorption or emission of one photon. On the time scale that we are using, the laser frequency is ω/ϵ^2, and the effective Planck constant is ϵ^2, so intuitively, a laser photon has energy ω.

3. We shall see that $FC_\epsilon(n,\,m)$ is significantly large only when $E_{\mathcal{B},n}-E_{\mathcal{B}}(a_{\mathcal{A}}) \;=\; O(\epsilon)$. Since level spacings in the $E_{\mathcal{B}}$ well are $O(\epsilon^2)$, the number of levels that get significantly excited is $O(\epsilon^{-1})$.

4. Intuitively, for small ϵ, each approximate nuclear bound state $\psi_{n,\epsilon}$ or ϕ_m is concentrated in an $O(\epsilon)$ neighborhood of a classical path in phase space. For the Franck–Condon factor to be significantly large, the two classical paths must have some places in phase space where they are within an $O(\epsilon)$ distance of one another. For ϕ_m, the path is an ellipse with major axes on the order of $\sqrt{m}\,\epsilon$, so the place where the paths are close to one another must be near $a_{\mathcal{A}}$, and near a turning point of the path for $\psi_{n,\epsilon}$ if $E_{\mathcal{B}}'(a_{\mathcal{A}}) \neq 0$.

5. When $m>0$, $|FC_\epsilon(n,\,m)|$ can fluctuate and have zeros in n near the values where $G_\epsilon(n,\,m)$ is large. Also, our formula (3.1) predicts that $|FC_\epsilon(n,\,m)|$ has two largest peaks with a energy separation of order $\sqrt{m}\;\epsilon$.

6. If $a_{\mathcal{B}} \;=\; a_{\mathcal{A}}$, where $a_{\mathcal{B}}$ is a local minimum of $E_{\mathcal{B}}$ with $E_{\mathcal{B}}''(a_{\mathcal{B}}) > 0$, the formulas for $FC_\epsilon(n,\,m)$ are just simplifications of the result of Proposition 7 of [10] that result from choosing the A and B to be real. This yields formula (3.2).

7. If $a_{\mathcal{B}} = a_{\mathcal{A}}$ and $E_{\mathcal{A}}''(a_{\mathcal{A}}) = E_{\mathcal{B}}''(a_{\mathcal{A}})$, then formula (3.2) has only one non-zero term, and

$FC(n,\, m) = \delta_{n,m}$.

To prove Theorem 3.1, we begin by solving the Schrödinger equation to zeroth order in ϵ and first order in μ.

The leading term has order $\epsilon^0\,\mu^0$. It equals

$$e^{i\,S_{\mathcal{A}}(t)/\epsilon^2}\ \phi_m(A_{\mathcal{A}}(t), B_{\mathcal{A}}(t), \epsilon^2, a_{\mathcal{A}}, 0, x)\ \Phi_{\mathcal{A}}(x),$$

We note that $S_{\mathcal{A}}(t) \,=\, -\,(t-t_0)\,E_{\mathcal{A},m}$, $A_{\mathcal{A}}(t) \,=\, e^{i\omega_{\mathcal{A}}(t-t_0)}/\omega_{\mathcal{A}}$ and $B_{\mathcal{A}}(t) \,=\, \omega_{\mathcal{A}}\,e^{i\omega_{\mathcal{A}}(t-t_0)}$ so that $B_{\mathcal{A}}(t)/A_{\mathcal{A}}(t) \,=\, \omega_{\mathcal{A}}^2$ is constant.

The order $\epsilon^0\,\mu^1$ term equals

$$\begin{aligned}
& -\,i\,\frac{\mu}{\epsilon^2}\,\int_{t_0}^t\,U_{BO}(t,\,s)\ X\ f(s,\,\epsilon)\ U_{BO}(s,t_0)\ \psi_0(t_0)\ ds \\
= \ & -\,i\,\frac{\mu}{\epsilon^2}\,\int_{t_0}^t\,f(s,\,\epsilon)\ U_{BO}(t,\,s)\ e^{i\,S_{\mathcal{A}}(s)/\epsilon^2}\,\phi_m(A_{\mathcal{A}}(s), B_{\mathcal{A}}(s), \epsilon^2, a_{\mathcal{A}}, 0, x)\ X\ \Phi_{\mathcal{A}}(x)\ ds \\
= \ & -\,i\,\frac{\mu}{\epsilon^2}\,\int_{t_0}^t\,f(s,\,\epsilon)\ U_{BO}(t,\,s)\ e^{i\,S_{\mathcal{A}}(s)/\epsilon^2}\,\phi_m(A_{\mathcal{A}}(s), B_{\mathcal{A}}(s), \epsilon^2, a_{\mathcal{A}}, 0, x) \\
& \quad \times\ \Big[\Phi_{\mathcal{A}}(x)\,\langle\,\Phi_{\mathcal{A}}(x),\,X\,\Phi_{\mathcal{A}}(x)\,\rangle_{\mathcal{H}_{\mathrm{el}}} + \,\Phi_{\mathcal{B}}(x)\,\langle\,\Phi_{\mathcal{B}}(x),\,X\,\Phi_{\mathcal{A}}(x)\,\rangle_{\mathcal{H}_{\mathrm{el}}} + \,P_\perp(x)\,X\,\Phi_{\mathcal{A}}(x)\Big]\ ds.
\end{aligned}$$

Here $P_\perp(x)$ denotes the projection in the electronic Hilbert space onto the subspace orthogonal to $\Phi_{\mathcal{A}}(x)$ and $\Phi_{\mathcal{B}}(x)$.

We now define $X_{\mathcal{A}\mathcal{A}}(x) \,=\, \langle\,\Phi_{\mathcal{A}}(x),\,X\,\Phi_{\mathcal{A}}(x)\,\rangle_{\mathcal{H}_{\mathrm{el}}}$ and $X_{\mathcal{B}\mathcal{A}}(x) \,=\, \langle\,\Phi_{\mathcal{B}}(x),\,X\,\Phi_{\mathcal{A}}(x)\,\rangle_{\mathcal{H}_{\mathrm{el}}}$. Then our last expression can be written as

$$-\,i\,\frac{\mu}{\epsilon^2}\,\int_{t_0}^t\,f(s,\,\epsilon)\ U_{BO}(t,\,s)\ e^{i\,S_{\mathcal{A}}(s)/\epsilon^2}\,\phi_m(A_{\mathcal{A}}(s), B_{\mathcal{A}}(s), \epsilon^2, a_{\mathcal{A}}, 0, x) \qquad (3.4)$$

$$\times\quad [\ X_{\mathcal{A}\mathcal{A}}(x)\ \Phi_{\mathcal{A}}(x)\ +\ X_{\mathcal{B}\mathcal{A}}(x)\ \Phi_{\mathcal{B}}(x)\ +\ P_\perp(x)\ X\ \Phi_{\mathcal{A}}(x)\ ]\ ds$$

$$=\ -\,i\,\frac{\mu}{\epsilon^2}\,\int_{t_0}^t\,f(s,\,\epsilon)\ U_{BO}(t,\,s)\ e^{i\,S_{\mathcal{A}}(s)/\epsilon^2}\,\phi_m(A_{\mathcal{A}}(s), B_{\mathcal{A}}(s), \epsilon^2, a_{\mathcal{A}}, 0, x) \qquad (3.5)$$

$$\times\quad [\ X_{\mathcal{A}\mathcal{A}}(a_{\mathcal{A}})\ \Phi_{\mathcal{A}}(x)\ +\ X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\ \Phi_{\mathcal{B}}(x)\ +\ P_\perp(x)\ X\ \Phi_{\mathcal{A}}(x)\ +\ O(\epsilon)\ ]\ ds.$$

We concentrate on the components of this expression that are in the $\Phi_{\mathcal{A}}(x)$ and $\Phi_{\mathcal{B}}(x)$ directions in the electronic Hilbert space. To leading order in ϵ, they are

$$-\, i\, \frac{\mu}{\epsilon^2}\, X_{\mathcal{A}\mathcal{A}}(a_{\mathcal{A}})\, e^{i\, S_{\mathcal{A}}(t)/\epsilon^2}\, \phi_m(A_{\mathcal{A}}(t), B_{\mathcal{A}}(t), \epsilon^2, a_{\mathcal{A}}, 0, x)\, \Phi_{\mathcal{A}}(x)\, \int_{t_0}^{t} f(s,\, \epsilon)\, ds \tag{3.6}$$

$$-\, i\, \frac{\mu}{\epsilon^2}\, X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\, \Phi_{\mathcal{B}}(x)\, \int_{t_0}^{t} f(s,\, \epsilon)\, e^{i\, S_{\mathcal{B}}(t,s)/\epsilon^2}\, \phi_m(A_{\mathcal{B}}(t,s), B_{\mathcal{B}}(t,s), \epsilon^2, a_{\mathcal{B}}(t,s), \eta_{\mathcal{B}}(t,s), x)\, ds$$

In this expression, $a_{\mathcal{B}}(t,s)$, $\eta_{\mathcal{B}}(t,s)$, etc. are determined by using the dynamics associated with level $E_{\mathcal{A}}$ for times between t_0 and s, and then the dynamics associated with the $E_{\mathcal{B}}$ level for times between s and t. Intuitively, the vertical transition takes place at time s.

Remarks.

1. This last step is where the errors occur in [11, 12]. Although it is buried in the notation, [11] and [12] have $X_{\mathcal{A}\mathcal{A}}(x)$ and $X_{\mathcal{B}\mathcal{A}}(x)$ outside the integrals instead of $X_{\mathcal{A}\mathcal{A}}(a_{\mathcal{A}})$ and $X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})$. These papers inadvertently commute the $U_{BO}(t,s)$ past the multiplication operators $X_{\mathcal{A}\mathcal{A}}(x)$ and $X_{\mathcal{B}\mathcal{A}}(x)$. Without correction, these errors yield an incorrect factor for the transition amplitude in the second line of (3.6) in generic situations, *i.e.*, when $\eta_{\mathcal{B}}(t)$ is not identically zero and $X_{\mathcal{B}\mathcal{A}}(x)$ is not constant.

2. We have been somewhat careless about the error term near the end of formula (3.5). For $f(t,\, \epsilon) \;=\; \epsilon^q\, f_0\,(\, t/\epsilon^{2-q}\,)\, \cos(\omega\, t/\epsilon^2)$, the rapid oscillations of the integrands yield $O(\mu)$ results in (3.5), despite the presence of the factor of ϵ^{-2}. By including more Taylor series terms in going from (3.4) to (3.5), one can show that our neglecting the error term in (3.5) produces corrections to (3.6) that are $O(\mu\, \epsilon)$. In several expressions below, we are similarly imprecise to avoid uninteresting technicalities.

3. If $f(t,\, s) \;=\; \epsilon^q\, f_0\,(\, t/\epsilon^{2-q}\,)\, \cos(\omega\, t/\epsilon^2)$, with f_0 smooth and $\omega \neq 0$, the first term in (3.6) is very small as ϵ goes to zero when $t \,>\,$ sup supp f_0, since the Fourier transform of f_0 decays rapidly.

Next, we expand the second term of (3.6) in terms of the nuclear vibrational states of the upper electronic level. We approximate the expansion coefficients by taking the inner product of (3.6) with the leading order quasimodes $\psi_{n,\epsilon}(x)\, \Phi_{\mathcal{B}}(x)$.

The electronic part of the inner product is trivial, so we just obtain a nuclear variable inner product:

$$\langle\, \psi_{n,\epsilon}(x)\, \Phi_{\mathcal{B}}(x),\ (\,\text{Formula (3.6)}\,)\, \rangle_{\text{all variables}}$$

$$\begin{aligned}
= \quad & -\, i\, \frac{\mu}{\epsilon^2}\, X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}}) \\
& \times \quad \int_{t_0}^{t} f(s,\,\epsilon)\, \langle\, \psi_{n,\epsilon}(x),\ e^{i\,S_{\mathcal{B}}(t,s)/\epsilon^2}\, \phi_m(A_{\mathcal{B}}(t,s), B_{\mathcal{B}}(t,s), \epsilon^2, a_{\mathcal{B}}(t,s), \eta_{\mathcal{B}}(t,s), x)\, \rangle\, ds \\
& + \quad O(\mu\, \epsilon) \\
= \quad & -\, i\, \frac{\mu}{\epsilon^2}\, X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}}) \\
& \times \quad \int_{t_0}^{t} f(s,\,\epsilon)\, \langle\, \psi_{n,\epsilon}(x),\ e^{-i(t-s)H_{\mathcal{B}}(\epsilon)/\epsilon^2}\ e^{i\,S_{\mathcal{A}}(s)/\epsilon^2}\, \phi_m(A_{\mathcal{A}}(s), B_{\mathcal{A}}(s), \epsilon^2, a_{\mathcal{A}}, 0, x)\, \rangle\, ds \\
& + \quad O(\mu\, \epsilon)
\end{aligned}$$

where $H_{\mathcal{B}}(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial x^2} \,+\, E_{\mathcal{B}}(x)$ has approximate eigenvector $\psi_{n,\epsilon}$ associated with $E_{\mathcal{B},n}$.

Hence, using the explicit formulas $A_{\mathcal{A}}(s) = A_{\mathcal{A}}\, e^{i\,\omega\,(s-t_0)}$, $B_{\mathcal{A}}(s) = B_{\mathcal{A}}\, e^{i\,\omega\,(s-t_0)}$ and the definition (2.2),

$$\langle\, \psi_{n,\epsilon}(x)\, \Phi_{\mathcal{B}}(x),\ (\,\text{Formula (3.6)}\,)\, \rangle_{\text{all variables}}$$

$$\begin{aligned}
= \quad & -\, i\, \mu\, X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\, e^{-i(t-t_0)E_{\mathcal{B},n}/\epsilon^2}\, \langle\, \psi_{n,\epsilon}(x),\ \phi_m(A_{\mathcal{A}}(t_0), B_{\mathcal{A}}(t_0), \epsilon^2, a_{\mathcal{A}}, 0, x)\, \rangle \\
& \qquad \times \quad \int_{t_0}^{t} f(s,\,\epsilon)\, e^{i(s-t_0)(E_{\mathcal{B},n}(\epsilon)-E_{\mathcal{A}}(a_{\mathcal{A}}))/\epsilon^2}\ e^{-i(s-t_0)(m+1/2)\omega_{\mathcal{A}}}\, \frac{ds}{\epsilon^2} \quad + \quad O(\mu\, \epsilon).
\end{aligned}$$

Thus,

$$\begin{aligned}
& \langle\, \psi_{n,\epsilon}(x)\, \Phi_{\mathcal{B}}(x),\ (\,\text{Formula (3.6)}\,)\, \rangle_{\text{all variables}} \\
& \quad = \; -\, i\, \mu\, X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\, e^{-i(t-t_0)E_{\mathcal{B},n}/\epsilon^2}\ FC_{\epsilon}(n,\, m) \\
& \qquad\qquad\qquad\qquad \times \quad \int_{t_0}^{t} f(s,\,\epsilon)\, e^{i(s-t_0)(E_{\mathcal{B},n}(\epsilon)-E_{\mathcal{A},m})/\epsilon^2}\, \frac{ds}{\epsilon^2} \\
& \qquad + \quad O(\mu\, \epsilon),
\end{aligned} \tag{3.7}$$

where $\quad FC_\epsilon(n,\, m) \;=\; \langle\, \psi_{n,\epsilon}(x),\; \phi_m(A_{\mathcal{A}}, B_{\mathcal{A}}, \epsilon^2, a_{\mathcal{A}}, 0, x)\, \rangle$.

Remark. If we choose $f(t,\, \epsilon) \;=\; \epsilon^{-q}\, f_0\,(\, t/\epsilon^{2-q}\,)\, \cos\,(\omega\, t/\epsilon^2)$ with $0 \le q \le 2$, we can say more about our last expression for the transition amplitude. We assume f_0 is a smooth function of compact support, and we look at our final expression for $t_0 < \inf\, \mathrm{supp}\, f(\,\cdot\,,\, \epsilon)$ and $t > \sup\, \mathrm{supp}\, f(\,\cdot\,,\, \epsilon)$. Asymptotically for small ϵ, we obtain

$$
\begin{aligned}
&-\, i\, \sqrt{\pi/2}\; \mu\; X_{\mathcal{B}\mathcal{A}}(a_{\mathcal{A}})\; e^{-itE_{\mathcal{B},n}/\epsilon^2}\; e^{it_0E_{\mathcal{A},m}/\epsilon^2}\; FC_\epsilon(n,\, m) \\
&\qquad \times\; \left[\; \widehat{f_0}\left(\frac{E_{\mathcal{A},m} - E_{\mathcal{B},n}(\epsilon) + \omega}{\epsilon^q}\right) \;+\; \widehat{f_0}\left(\frac{E_{\mathcal{A},m} - E_{\mathcal{B},n}(\epsilon) - \omega}{\epsilon^q}\right)\;\right]. \qquad (3.8)
\end{aligned}
$$

This proves formula (3.3) of Theorem 3.1.

We now give the leading order expression in ϵ for $FC_\epsilon(n,\, m)$. In this discussion, estimates are not uniform in m, so we assume it is fixed.

Using (2.10) to represent $\psi_{n,\,\epsilon}(x)$, we write $FC_\epsilon(n,\, m)$ as

$$
\pi^{-1/4}\, \epsilon^{-1/2}\, \sqrt{\frac{|\theta|}{2\,\tau(E)}}\; \int_{-\tau(E)/2}^{\tau(E)/2}\; e^{i\left(S(r)+rE+r\frac{\pi\epsilon^2}{\tau(E)}\right)/\epsilon^2}\; g(r,\, \epsilon)\; dr \;+\; O(\epsilon),
$$

where

$$
g(r,\, \epsilon) \;=\; \langle\, \phi_0(A(r), B(r), \epsilon^2, a(r), \eta(r), x),\; \phi_m(A_{\mathcal{A}}, B_{\mathcal{A}}, \epsilon^2, a_{\mathcal{A}}, 0, x)\,\rangle.
$$

The following lemma implies that $g(r,\, \epsilon)$ is large only when $(a(r) - a_{\mathcal{A}})$ and $\eta(r)$ are $O(\epsilon^2)$.

Lemma 3.1 *Suppose the pair $(A(r),\, B(r))$ is restricted to a compact set on which* $\mathrm{Re}\, \left(\, \overline{B(r)}\, A(r)\,\right) \;=\; 1$ *is satisfied. Then*

$$
|g(r,\, \epsilon)| \;\le\; C_1\, \exp\left(-\, \frac{C_2\; (\,(a(r) - a_{\mathcal{A}})^2 + \eta(r)^2\,)}{\epsilon^2}\right),
$$

where $C_1 > 0$ and $C_2 > 0$.

Proof: This is essentially contained in Propositions 4 and 7 of [10]. ∎

It follows from this lemma that if $E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) \gg \epsilon^2$, then $FC_\epsilon(n,\, m)$ is bounded by $\exp(-c/\epsilon^p)$ for some $c>0$ and $p>0$. So, we choose $E_{\mathcal{B},n}$ near $E_{\mathcal{B}}(a_{\mathcal{A}})$ in order for $FC_\epsilon(n,\, m)$ to be significantly large. This choice restricts a_0 to a small compact neighborhood of $a_{\mathcal{A}}$. It follows that for all orbits we choose, $A(r)$ and $B(r)$ will lie in compact sets as in Lemma 3.1. So, the only significant contribution to the integral comes from values of r that satisfy $|r| < \epsilon^{1-\delta}$, where $\delta > 0$ is arbitrarily small.

For such values of r, we have

$$a(r) \;=\; a_0 \;-\; E_{\mathcal{B}}'(a_0)\, r^2/2 \;+\; O(\epsilon^{3-3\delta}), \tag{3.9}$$

$$\eta(r) \;=\; -\, E_{\mathcal{B}}'(a_0)\, r \;+\; O(\epsilon^{2-2\delta}), \tag{3.10}$$

$$A(r) \;=\; A_{\mathcal{A}} \;+\; i\, r\, B_{\mathcal{A}} \;+\; O(\epsilon^{2-2\delta}), \tag{3.11}$$

$$B(r) \;=\; B_{\mathcal{A}} \;+\; i\, r \left[E_{\mathcal{B}}''(a_0) \;+\; 2\,\alpha(E)\,(E_{\mathcal{B}}'(a_0))^2\right] A_{\mathcal{A}} \;+\; O(\epsilon^{2-2\delta}), \tag{3.12}$$

$$S(r) \;=\; -\, r\, E_{\mathcal{B}}(a_0) \;+\; O(\epsilon^{3-3\delta}). \tag{3.13}$$

We now use the formulas from Propositions 4 and 7 of [10] to write

$$\begin{aligned} g(r,\, \epsilon) \;=\;& \frac{2^{-(m-1)/2}}{\sqrt{m!}} \left(\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}}\right)^{-(m+1)/2} \left(\overline{B(r)}\, A_{\mathcal{A}} - \overline{A(r)}\, B_{\mathcal{A}}\right)^{m/2} \\ &\times\; H_m\left(\epsilon^{-1}\, \frac{\overline{B(r)}(a(r)-a_{\mathcal{A}}) \;-\; i\,\overline{A(r)}\,\eta(r)}{\sqrt{(\overline{B(r)}\, A_{\mathcal{A}} - \overline{A(r)}\, B_{\mathcal{A}})\;(\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}})}}\right) \\ &\times\; \exp\left(-\,\frac{\overline{A(r)}\, A_{\mathcal{A}}\,\eta(r)^2 + \overline{B(r)}\, B_{\mathcal{A}}\,(a(r)-a_{\mathcal{A}})^2}{2\;(\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}})\;\epsilon^2} \;+\; i\,\frac{\overline{A(r)}\, B_{\mathcal{A}}\,\eta(r)\,(a(r)-a_{\mathcal{A}})}{(\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}})\;\epsilon^2}\right). \end{aligned}$$

Lemma 3.2 *For $|r| < \epsilon^{1-\delta}$, and $|a_0 - a_{\mathcal{A}}| < \epsilon^{1-\delta}$, with $\delta < 1/(m+1)$, we have*

$$\left(\frac{\overline{B(r)}\, A_{\mathcal{A}} - \overline{A(r)}\, B_{\mathcal{A}}}{\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}}}\right)^{m/2} H_m\left(\epsilon^{-1}\, \frac{\overline{B(r)}(a(r)-a_{\mathcal{A}}) \;-\; i\,\overline{A(r)}\,\eta(r)}{\sqrt{(\overline{B(r)}\, A_{\mathcal{A}} - \overline{A(r)}\, B_{\mathcal{A}})\;(\overline{B(r)}\, A_{\mathcal{A}} + \overline{A(r)}\, B_{\mathcal{A}})}}\right)$$

$$= \quad \left(\epsilon^{-1} \, (\overline{B(r)}(a(r) - a_{\mathcal{A}}) \, - \, i \, \overline{A(r)} \, \eta(r)) \right)^m \quad + \quad O\left(\epsilon^{1-(m+1)\delta} \right).$$

Proof: We write the Hermite polynomial in the lemma as $H_m(z) \, = \, \sum_{j=0}^{m} c_j \, z^j$. The $j = m$ term is

$$\frac{2^m}{(\overline{B(r)} \, A_{\mathcal{A}} \, + \, \overline{A(r)} \, B_{\mathcal{A}})^m} \; \left(\epsilon^{-1} \, (\overline{B(r)}(a(r) - a_{\mathcal{A}}) \, - \, i \, \overline{A(r)} \, \eta(t)) \right)^m$$
$$= \; \left(\epsilon^{-1} \, (\overline{B(r)}(a(r) - a_{\mathcal{A}}) \, - \, i \, \overline{A(r)} \, \eta(r)) \right)^m \quad + \quad O\left(\epsilon^{1-(m+1)\delta} \right).$$

This yields the expression displayed explicitly on the right hand side in the lemma. Another error term comes from the remaining terms in the polynomial.

For $j < m$, we use the asymptotics (3.9)–(3.12) and the fact that both $A_{\mathcal{A}}$ and $B_{\mathcal{A}}$ are real. After some calculation, we see that the sum of these terms equals

$$\sum_{j=0}^{m-1} \, 2^{-\frac{m+j}{2}} \; (1 \, + \, O(r)) \; c_j \; (K \, r \, + \, O(r^2))^{\frac{m-j}{2}} \left(\frac{B_{\mathcal{A}} \, (a_0 - a_{\mathcal{A}}) \, + \, O(r)}{\epsilon} \right)^j,$$

where $K \, = \, i \left(B_{\mathcal{A}}^2 - \left[E_{\mathcal{B}}''(a_0) + 2\alpha(E)(E_{\mathcal{B}}'(a_0))^2 \right] A_{\mathcal{A}}^2 \right)$.

We now simply estimate each term in this sum when $|r| < \epsilon^{1-\delta}$ and $|a_0 - a_{\mathcal{A}}| < \epsilon^{1-\delta}$. For small ϵ, the largest term has $j = m-2$, since $c_{m-1} = 0$. This term equals

$$2^{-m+1} \, c_{m-2} \, (K \, r \, + \, O(r^2)) \, \left(\frac{B_{\mathcal{A}}(a_0 - a_{\mathcal{A}}) \, + \, O(r)}{\epsilon} \right)^{m-2} \; = \; 2^{-m+1} \, c_{m-2} \, O(\epsilon^{1-\delta}) \, O(\epsilon^{-(m-2)\delta}).$$

This implies the lemma. ∎

With this lemma, $B_{\mathcal{A}} \, A_{\mathcal{A}} = 1$, and (3.9)–(3.12), some tedious, but straightforward calculations show that for small δ and $|r| < \epsilon^{1-\delta}$,

$$g(r, \epsilon) \;\; = \;\; \left(\frac{2^{-m} \, \epsilon^{-m}}{\sqrt{m!}} \, \left(B_{\mathcal{A}} \, (a_0 - a_{\mathcal{A}}) \, + \, i \, A_{\mathcal{A}} \, E_{\mathcal{B}}'(a_0) \, r \right)^m + \, O\,(\, \epsilon^p \,) \right) \tag{3.14}$$
$$\times \;\; \exp\left(- \, \frac{B_{\mathcal{A}}^2 \, (a_0 - a_{\mathcal{A}})^2}{4 \, \epsilon^2} \, - \, \frac{A_{\mathcal{A}}^2 \, (E_{\mathcal{B}}'(a_0))^2 \, r^2}{4 \, \epsilon^2} \, - \, \frac{i \, A_{\mathcal{A}} \, B_{\mathcal{A}} \, E_{\mathcal{B}}'(a_0) \, (a_0 - a_{\mathcal{A}}) \, r}{2 \, \epsilon^2} \right).$$

where $p > 0$ (and can be chosen arbitrarily close to 1 if δ is small enough).

We can now evaluate the leading asymptotics for $FC_\epsilon(n, m)$. We first restrict the r integration region to $|r| < \epsilon^{1-\delta}$, then substitute the above asymptotics for g. Then we extend the integration to all r, again making an exponentially small error. We can then evaluate the integral explicitly ([4] page 382, formula 3.462.4) to obtain

$$\begin{aligned} FC_\epsilon(n, m) \;&=\; \frac{\pi^{1/4}\, 2^{-(m-1)/2}\ \epsilon^{1/2}}{\sqrt{m!\ \tau(E)\, |E_{\mathcal{B}}'(a_0)|\, A_{\mathcal{A}}}}\ H_m\left(\frac{B_{\mathcal{A}}\,(a_0 - a_{\mathcal{A}})}{\epsilon}\right)\ \exp\left(-\ \frac{B_{\mathcal{A}}^2\ (a_0 - a_{\mathcal{A}})^2}{2\,\epsilon^2}\right). \\ &\quad +\ O\left(\epsilon^{1/2+p}\right). \end{aligned} \tag{3.15}$$

To get the error estimate, here, we actually include some of the error term from (3.14) to get easy bounds. We then observe that including these terms yields corrections that are themselves $O\left(\epsilon^{1/2+p}\right)$. These corrections are small because of oscillations in the integral, and we have dropped them in (3.15).

Expression (3.15) is only significant if $a_0 - a_{\mathcal{A}} \;=\; O(\epsilon)$. This condition is equivalent to $E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) \;=\; O(\epsilon)$. Since level spacings in the $E_{\mathcal{B}}$ well are $O(\epsilon^2)$, the number of levels that get significantly excited is $O(\epsilon^{-1})$.

Furthermore, since $E_{\mathcal{B},n} = E_{\mathcal{B}}(a_0) + \frac{\pi\epsilon^2}{\tau(E)} + O(\epsilon^3)$ and $E_{\mathcal{B}}(a_0) - E_{\mathcal{B}}(a_{\mathcal{A}}) = E_{\mathcal{B}}'(a_{\mathcal{A}})(a_0 - a_{\mathcal{A}}) + O((a_0 - a_{\mathcal{A}})^2)$,

$$\begin{aligned} FC_\epsilon(n, m) \;&=\; \frac{\pi^{1/4}\, 2^{-(m-1)/2}\ \epsilon^{1/2}}{\sqrt{m!\ \tau(E)\, |E_{\mathcal{B}}'(a_0)|\, A_{\mathcal{A}}}}\ H_m\left(\frac{B_{\mathcal{A}}\left(E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) - \frac{\pi\epsilon^2}{\tau(E)}\right)}{|E_{\mathcal{B}}'(a_{\mathcal{A}})|\,\epsilon}\right) \\ &\quad \times\ \ \exp\left(-\ \frac{B_{\mathcal{A}}^2\ \left(E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) - \frac{\pi\epsilon^2}{\tau(E)}\right)^2}{2\,E_{\mathcal{B}}'(a_{\mathcal{A}})^2\,\epsilon^2}\right)\ +\ O(\epsilon^{1/2+p}), \end{aligned}$$

for some $p > 0$.

Remarks.

1. The Franck–Condon factors are small unless $E \;=\; E_{\mathcal{B}}(a_0) \;\approx\; E_{\mathcal{B},n} \;\approx\; E_{\mathcal{B}}(a_{\mathcal{A}})$. Since various quantities depend continuously on the energy, we have

$$FC_\epsilon(n, m) \;=\; \frac{\pi^{1/4}\, 2^{-(m-1)/2}\ \epsilon^{1/2}}{\sqrt{m!\ \tau(E_{\mathcal{B}}(a_{\mathcal{A}}))\, |E_{\mathcal{B}}'(a_{\mathcal{A}})|\, A_{\mathcal{A}}}}\ H_m\left(\frac{B_{\mathcal{A}}\left(E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) - \frac{\pi\epsilon^2}{\tau(E_{\mathcal{B}}(a_{\mathcal{A}}))}\right)}{|E_{\mathcal{B}}'(a_{\mathcal{A}})|\,\epsilon}\right)$$

$$\times \quad \exp\left(- \frac{B_{\mathcal{A}}^2 \ \left(E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) - \frac{\pi\epsilon^2}{\tau(E_{\mathcal{B}}(a_{\mathcal{A}}))} \right)^2}{2\, E'_{\mathcal{B}}(a_{\mathcal{A}})^2\, \epsilon^2} \right) \ + \ O(\epsilon^{1/2+p}),$$

when $E_{\mathcal{B},n} - E_{\mathcal{B}}(a_{\mathcal{A}}) \ = \ O(\epsilon)$.

2. The Franck–Condon factors arise from expanding a normalized wave packet in an orthonormal basis. So, if we sum their absolute squares over n, we must get 1. We can observe this from our formulas. The Bohr–Sommerfeld conditions require $I(E_{\mathcal{B},n+1}) - I(E_{\mathcal{B},n}) \approx 2\pi\epsilon^2$. Thus, $\dfrac{\partial I}{\partial E}\,\Delta E \ \approx \ 2\pi\epsilon^2$, and hence, $\Delta E \ \approx \ \dfrac{2\pi\epsilon^2}{\tau(E)}$. Therefore,

$$\begin{aligned}
\sum_n |FC_\epsilon(n,\,m)|^2 \ &\approx \ \frac{1}{\Delta E} \int |FC_\epsilon(n(\mathcal{E}),\,m)|^2 \ d\mathcal{E} \\
&\approx \ \frac{\tau(E)}{2\,\pi\,\epsilon^2} \ \frac{\pi^{1/2}\ 2^{-(m-1)}\ \epsilon}{m!\ \tau(E)\,|E'_{\mathcal{B}}(a_{\mathcal{A}})|\,A_{\mathcal{A}}} \\
&\quad \times \ \int H_m\left(\frac{B_{\mathcal{A}}\,(\mathcal{E} - E_{\mathcal{B}}(a_{\mathcal{A}}))}{|E'_{\mathcal{B}}(a_{\mathcal{A}})|\,\epsilon} \right)^2 \exp\left(- \frac{B_{\mathcal{A}}^2\,(\mathcal{E} - E_{\mathcal{B}}(a_{\mathcal{A}}))^2}{|E'_{\mathcal{B}}(a_{\mathcal{A}})|^2\,\epsilon^2} \right) \ d\mathcal{E} \\
&= \ \frac{2^{-m}\ \pi^{-1/2}}{m!} \ \int \ H_m(z)^2\ e^{-z^2}\ dz \\
&= \ 1.
\end{aligned}$$

4 Expansions to all orders in ϵ and μ

Since our main results do not depend on this section, we do not provide many details that can be found elsewhere. We restrict attention to the situation where the electron Hamiltonian has finitely many levels that never cross one another. A more general situation is discussed in [11, 12], but identifying and correcting the error is the same.

The basic idea for correcting the results (Theorems 3.2 and 3.3) of [12] is to redefine and take superpositions of the functions $\Psi_{(i,k_1,\ldots,k_m),n}(\epsilon, s_1, \ldots, s_m, t)$ that appear in these theorems. Their definitions are described near the end of Section 3.2 of [12], but they are not written out explicitly. However, the dependence of these functions on the multi-index j for the semiclassical wave packets is suppressed in [11, 12]. When the correction is made, we cannot omit this dependence because there is some mixing of different values of j.

Throughout this discussion, the value of $n \geq 0$ is fixed. We do all calculations modulo ϵ^{n+1} errors and perform a perturbation expansion in powers of μ.

We begin this discussion with some preliminary results. There are explicit constructions of asymptotic expansions for solutions to (2.1) when $\mu = 0$ that can be found in [5, 7, 8]. For any electronic level i and any multi-index j, the constructions in [5, 7, 8] yield a unique approximate solution $\psi_{n,i,j}(x,\, t,\, s)$ to (2.1) with $\mu = 0$, subject to the condition that

$$\langle\, \Phi_i(x),\, \psi_{n,i,j}(x,\, s,\, s)\,\rangle_{\mathcal{H}_{\rm el}} \;=\; e^{iS_i(s)/\epsilon^2}\,\phi_j(A_i(s), B_i(s), \epsilon^2, a_i(s), \eta_i(s), x).$$

The dynamics of $A_i(t)$, $B_i(t)$, $a_i(t)$, $\eta_i(t)$ and $S_i(t)$ are determined by the $i^{\rm th}$ electronic level.

The function $\psi_{n,i,j}(x,\, t,\, s)$ is a time–dependent finite sum of the form

$$\psi_{n,i,j} \;=\; e^{iS_i/\epsilon^2}\left(\Phi_i(x)\,\phi_j(x) \;+\; \sum_{p=1}^{n+2}\epsilon^p \sum_{k,j'} f_{p,k,j'}(x,\, t)\,\Phi_k(x)\,\phi_{j'}(x)\right).$$

For each t, we approximate each $f_{p,k,j'}(x,\, t)$ by its Taylor series in $(x - a(t))$ of order $\max\{n-p,\, 0\}$. This adds an $O(\epsilon^{n+1})$ error. When this Taylor series multiplies $\phi_{j'}$, the product can be written as a finite linear combination of more $\phi_{j'}$, with $|j'-j| \leq 3\,\min\{p,\, n\} + \max\{n-p,\, 0\}$. Since $p \leq n+2$, this implies that up to an $O(\epsilon^{n+1})$ error $\psi_{n,i,j}(x,\, t,\, s)$ is a finite linear combination of $\Phi_k(x)\,\phi_{j'}(x)$ with $|j'-j| \leq 3n+4$.

Thus, modulo an $O(\epsilon^{n+1})$ error, $\psi_{n,i,j}$ is a time–dependent finite sum of the form

$$\psi_{n,i,j} \;=\; e^{iS_i/\epsilon^2}\left(\Phi_i(x)\,\phi_j(x) \;+\; \sum_{p=1}^{n+2}\epsilon^p \sum_{k,j'} c^{(0)}_{p,k,j'}(t)\,\Phi_k(x)\,\phi_{j'}(x)\right) \;+\; O(\epsilon^{n+1}). \quad (4.1)$$

In addition to this result, our arguments require that we be able to write any $\Phi_i(x)\,\phi_j(x)$ as a finite linear combination of the $\psi_{n,i'',j''}$ up to an $O(\epsilon^{n+1})$ error. To see that this can be done, we iteratively make use of expression (4.1). First, we rewrite (4.1) as

$$\begin{aligned} e^{-iS_i/\epsilon^2}\,\psi_{n,i,j} \;&=\; \Phi_i(x)\,\phi_j(x) \;+\; \epsilon \sum_{k,j'} c^{(0)}_{1,k,j'}(t)\,\Phi_k(x)\,\phi_{j'}(x) \\ &\quad+\; \sum_{p=2}^{n+2}\epsilon^p \sum_{k,j'} c^{(0)}_{p,k,j'}(t)\,\Phi_k(x)\,\phi_{j'}(x) \;+\; O(\epsilon^{n+1}). \end{aligned}$$

Then we use (4.1) again to rewrite the order ϵ terms as linear combinations of $\psi_{n,k,j'}$ plus higher order corrections. Thus, we see that

$$\begin{aligned} e^{-iS_i/\epsilon^2}\,\psi_{n,i,j} &= \Phi_i(x)\,\phi_j(x) \;+\; \epsilon\sum_{k,j'} c^{(0)}_{1,k,j'}(t)\,e^{-iS_k/\epsilon^2}\,\psi_{n,k,j'}(x) \\ &\quad + \sum_{p=2}^{n+2}\epsilon^p\sum_{k,j'} c^{(1)}_{p,k,j'}(t)\,\Phi_k(x)\,\phi_{j'}(x) \;+\; O(\epsilon^{n+1}), \end{aligned}$$

where the sums on the right hand side are finite. We now repeat this procedure to replace the $\Phi_k(x)\,\phi_{j'}(x)$ in the order ϵ^2 terms by $\psi_{n,k,j'}$ plus higher order corrections.

By repeating this process, we obtain

$$e^{-iS_i/\epsilon^2}\,\psi_{n,i,j} \;=\; \Phi_i(x)\,\phi_j(x) \;+\; \sum_{p=1}^{n+2}\epsilon^p\sum_{k,j'} c^{(p-1)}_{p,k,j'}(t)\,e^{-iS_k/\epsilon^2}\,\psi_{n,k,j'}(x) \;+\; O(\epsilon^{n+1}),$$

where the sums are finite.

It follows immediately that

$$\begin{aligned} \Phi_i(x)\,\phi_j(x) &= \left(e^{-iS_i/\epsilon^2}\,\psi_{n,i,j} \;-\; \sum_{p=1}^{n+2}\epsilon^p\sum_{k,j'} c^{(p-1)}_{p,k,j'}(t)\,e^{-iS_k/\epsilon^2}\,\psi_{n,k,j'}(x)\right) \\ &\quad + O(\epsilon^{n+1}), \end{aligned} \tag{4.2}$$

where the sums are finite.

With these preliminary facts established, we now turn to the main point of this section.

We fix the order n of the expansion in ϵ and the choice of the i^{th} initial electronic level. We also fix a value of the multi-index j that labels an initial semiclassical nuclear wave packet at time t_0.

Order 0 in μ. To zeroth order in μ and n^{th} order in ϵ, we have the approximate solution

$$\Psi_{n,i,j}(\epsilon,t) \;=\; \psi_{n,i,j}(x,\,t,\,t_0).$$

This is exactly as in [11, 12], although our notation is slightly different.

First Order in μ. To calculate the higher order corrections in μ, we use the Dyson expansion of [11, 12]. We let $U_{BO}^{(n)}(t,\, s_1)$ denote the Born–Oppenheimer propagator with error $O(\epsilon^{n+1})$. Then the first order term in μ is

$$
\begin{aligned}
& -\, i\, \frac{\mu}{\epsilon^2} \int_{t_0}^{t} f(s_1,\, \epsilon)\; U_{BO}^{(n)}(t,\, s_1)\; X\; U_{BO}^{(n)}(s_1, t_0)\; \psi_{n,i,j}(x,\, t_0,\, t_0)\; ds_1 \\
=\;\; & -\, i\, \frac{\mu}{\epsilon^2} \int_{t_0}^{t} f(s_1,\, \epsilon)\; U_{BO}^{(n)}(t,\, s_1)\; X\; \psi_{n,i,j}(x,\, s_1,\, t_0)\; ds.
\end{aligned} \tag{4.3}
$$

We use (4.1) to rewrite $\psi_{n,i,j}(x,\, s_1,\, t_0)$ as a finite linear combination

$$
\sum_{i',\; j'} \alpha_{i',j'}(s_1,\, \epsilon)\; \Phi_{i'}(x)\, \phi_{j'}(x) \;+\; O(\epsilon^{n+1}).
$$

The operator X applied to this yields another finite linear combination

$$
\sum_{i'',\; i',\; j'} \beta_{i'',i',j'}(s_1,\, \epsilon)\; \Phi_{i''}(x)\; X_{i'',i'}(x)\; \phi_{j'}(x) \;+\; O(\epsilon^{n+1}),
$$

where $X_{i'',i'}(x) \;=\; \langle\, \Phi_{i''},\, X\, \Phi_{i'} \,\rangle$. We make another $O(\epsilon^{n+1})$ error by replacing $X_{i'',i'}(x)$ by its n^{th} order Taylor series.

$$
\sum_{|m|\le n} \frac{(D^m X_{i'',i'})\, (a(s_1))\, (x - a(s_1))^m}{m!}.
$$

When this multiplies the $\phi_{j'}(x)$ we again obtain a finite linear combination

$$
\sum_{i'',\; j''} \gamma_{i'',j''}(s_1,\, \epsilon)\; \Phi_{i''}(x)\; \phi_{j''}(x) \;+\; O(\epsilon^{n+1}).
$$

We apply (4.2) to write this as

$$
X\, \psi_{n,i,j}(x,\, s_1,\, t_0) \;=\; \sum_{i_1,\; j_1} \zeta_{i_1,j_1}(\epsilon,\, s_1)\; \psi_{n,i_1,j_1}(x,\, s_1,\, s_1) \;+\; O(\epsilon^{n+1}),
$$

where the linear combination is finite.

We use this result in (4.3) and then do the Born–Oppenheimer propagation to obtain

$$
\begin{aligned}
& -\, i\, \frac{\mu}{\epsilon^2} \int_{t_0}^{t} f(s_1,\, \epsilon)\; U_{BO}^{(n)}(t,\, s_1)\; X\; \psi_{n.i,j}(x,\, s_1,\, t_0)\; ds_1 \\
=\;\; & \sum_{i_1,\; j_1} -\, i\, \frac{\mu}{\epsilon^2} \int_{t_0}^{t} f(s_1,\, \epsilon)\; \zeta_{i_1,j_1}(\epsilon,\, s_1) \psi_{n,i_1,j_1}(x,\, t,\, s_1)\; ds_1 \;+\; O(\epsilon^{n+1}).
\end{aligned} \tag{4.4}
$$

In order to get the proper error estimate here, we again use the assumed form of $f(s_1, \epsilon)$ to overcome the factor of $\frac{1}{\epsilon^2}$ as in Section 3.1.

Intuitively, the terms that have a given value of i_1 have made a jump at time s_1 from level i to level i_1, after which, they propagate according to the Born–Oppenheimer dynamics associated with level i_1. The sum over j_1 results from the nuclear wave packet changing somewhat when the jump occurs. Thus, the precise "vertical transition" intuition is only accurate to leading order in ϵ.

We can go to higher orders in μ by treating the higher order Dyson expansion terms in [11, 12] by the same technique. Where the operator X occurs in the formal expressions, we use (4.1) to rewrite everything as a finite linear combination of $\Phi_{i'}(x)\, \phi_{j'}(x)$. We then use Taylor series to expand $X_{i'',i'}(x)$. Then we use (4.2) to reexpress the result in terms of new basis vectors ψ_{n,i_k,j_k}

The order μ^m term makes m transitions between electronic levels at times $s_1,\, s_2,\, \cdots,\, s_m$ as expected. However, the $O(\epsilon^n)$–accurate wave function is an enormous sum of terms.

Remark. When $n = 0$, these expressions are much simpler. In particular, expression (4.4) reduces to

$$\sum_{i_1} -\, i\, \frac{\mu}{\epsilon^2}\, \Phi_{i_1}(x) \int_{t_0}^{t} f(s_1,\, \epsilon)\; X_{i_1,i}(a_i(s_1))\; e^{iS_{i_1,i}(t,s_1)/\epsilon^2}\; \phi_j(x,\, t,\, s_1)\; ds_1 \;+\; O(\epsilon).$$

Here the semiclassical wave packet $\phi_j(x,\, t,\, s_1)$ and the $S_{i_1,i}(t, s_1)$ propagate according to the dynamics of level i from time t_0 to time s_1 and the dynamics of level i_1 from time s_1 to time t. This differs from [11, 12] for $n = 0$ only in the presence of the factor $X_{i_1,i}(a_i(s_1))$ in the integrand.

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