Remarks on the Born-Oppenheimer approximation

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The Born-Oppenheimer formulas, as modified by the introduction of the adiabatic connection, are derived from the effective action obtained by integrating out the fast variables. The parallels and differences with Berry's approach are stressed, and the corrections to the approximation are investigated.

One of the time-honored applications of the adiabatic approximation is the well-known Born-Oppenheimer (BO) approximation.[1] Recently this approximation was reexamined in view of the developments originating from the results of Berry.[2] In this light the usual formulas are modified by the appearance of a gauge potential whose effect is to ensure invariance of the measurable quantities against a change of phases in the states used.

In this paper the BO results are derived from the formalism originally described by Berry.[3] The procedure is not immediate due to the fact that the usual BO Hamiltonian contains terms of higher order in $\hbar$ than those produced by the usual adiabatic approximation.

We will consider a system with two types of physically distinguishable coordinates: the "slow" ones, denoted by $\mathbf{Q}$; and the "fast" ones, denoted by $\mathbf{q}$. The corresponding canonical momenta will be denoted by $\mathbf{P}$ and $\mathbf{p}$, respectively. The classical example is a molecule where the $\mathbf{q}$ denote the electronic coordinates and the $\mathbf{Q}$ the nuclear ones. We will assume a total Hamiltonian of the form

$$H_T \equiv H_s(\mathbf{Q},\mathbf{P}) + H_f(\mathbf{q},\mathbf{p};\mathbf{Q}) \ ;$$

moreover we assume that the eigenfunctions of H_f, denoted by $|n(\mathbf{Q})\rangle$, are known and satisfy

$$H_f|n(\mathbf{Q})\rangle = E_n(\mathbf{Q})|n(\mathbf{Q})\rangle \ .$$

Note that both states and energies depend on $\mathbf{Q}$ as a parameter. The usual BO approximation consists in proposing $|\Psi_n\rangle \equiv \Phi(\mathbf{Q})|n(\mathbf{Q})\rangle$ as an ansatz for the complete wave function; then it is assumed that the fast variables do not suffer transitions from their instantaneous state so that a projection unto $|n\rangle$ is appropriate. In this manner one obtains the effective Hamiltonian found in Ref. 2, which describes the time evolution of Φ:

$$H^{(n)}_{\text{eff}}\Phi \equiv \langle n|H_T|\Psi_n\rangle \ .$$

We will not need the precise form of H_f. Regarding H_s, however, we will assume, for simplicity,

$$H_s = \frac{1}{2M}\mathbf{P}^2 + V_0(\mathbf{Q}) \ .$$

Substituting in the definition of $H^{(n)}_{\text{eff}}$ we get

$$H^{(n)}_{\text{eff}} = \frac{1}{2M}(\mathbf{P} - \hbar\mathbf{A}^{(n)})^2 + V^{(n)}_{\text{eff}} + V_0 \ ,$$

where

$$\mathbf{A}^{(n)} \equiv i\langle n|\nabla_{\mathbf{Q}}|n\rangle \ ,$$

$$V^{(n)}_{\text{eff}}(\mathbf{Q}) \equiv E_n(\mathbf{Q}) + \frac{\hbar^2}{2M}\left[\sum_a \left[\frac{\partial\langle n|}{\partial Q^a}\right]\left[\frac{\partial|n\rangle}{\partial Q^a}\right] - (\mathbf{A}^{(n)})^2\right] \ .$$

Such an expression for $H^{(n)}_{\text{eff}}$ corresponds to a Lagrangian

$$L^{(n)}_{\text{eff}} = \tfrac{1}{2}M\dot{\mathbf{Q}}^2 + \hbar\mathbf{A}^{(n)}\cdot\dot{\mathbf{Q}} - V^{(n)}_{\text{eff}}(\mathbf{Q}) - V_0(\mathbf{Q}) \ . \tag{1}$$

Note that $L^{(n)}_{\text{eff}}$ contains terms both linear and quadratic in $\hbar$.

The question we wish to address now is how to obtain the above expression for $L^{(n)}_{\text{eff}}$ using the approach developed by Berry. To this end we consider for the moment only the Hamiltonian H_f with $\mathbf{Q}$ a set slowly varying (in time) external fields. Then the time evolution of the state $|n\rangle$ is given by

$$|n,t\rangle = \exp\left[-\frac{i}{\hbar}\int_0^t E_n(\mathbf{Q}(t))dt + i\int_0^t \mathbf{A}^{(n)}\cdot\dot{\mathbf{Q}}\,dt\right]|n(\mathbf{Q}(t))\rangle \ , \tag{2}$$

which just expresses the usual adiabatic assumption that the evolution is given, up to a phase, by the instantaneous eigenvalues of the Hamiltonian. The first term in the exponent is the usual dynamic phase, the second term is the adiabatic phase, $\mathbf{A}^{(n)}$ being the adiabatic connection. Note that the above expression is useful even when $\mathbf{Q}(t) \neq \mathbf{Q}(0)$ as it is explicitly invariant under phase changes in the eigenstates of H_f.

In the following we will also need the corrections to this formula; the natural way of including these is to expand the state of the system at time t, denoted by $|t\rangle$, in the instantaneous eigenbasis of H_f,

$$|t\rangle = \sum_n c_n(t)|n,t\rangle \ , \tag{3}$$

with $|n,t\rangle$ defined in (2). Substituting in the time-dependent Schrödinger equation, we find that the c_n must obey

$$i\dot{c}_n(t) = \sum_m \mathcal{H}_{nm}(t)c_m(t) \ , \tag{4}$$

where

$$\mathcal{K}_{nm}=\begin{cases}-i\exp(-i\omega_{nm})\langle n|\dot{\mathbf{Q}}\cdot\nabla_{\mathbf{Q}}|m\rangle & \text{for } n\neq m;\\ 0 & \text{otherwise;}\end{cases}$$

$$\omega_{nm}\equiv\int_0^t\dot{\mathbf{Q}}\cdot(\mathbf{A}^{(n)}-\mathbf{A}^{(m)})dt-\frac{1}{\hbar}\int_0^t(E_n-E_m)dt\ .$$

Note that $\mathcal{K}=\mathcal{K}^\dagger$ and this implies we can take $\sum_k|c_k|^2=1$.

Since the fast variables, to lowest order, are assumed to remain in state $|n\rangle$, the appropriate initial conditions are $c_k(0)=\delta_{nk}$. Then the iterative solution of (4) yields

$$\begin{aligned}c_n(t)&=1-\int_0^t dt'\int_0^{t'}dt''\sum_l\mathcal{K}_{nl}(t')\mathcal{K}_{ln}(t'')+O(\mathcal{K}^3)\\&\simeq\exp\left[\int_0^t dt'\int_0^{t'}dt''\sum_l\mathcal{K}_{nl}(t')\mathcal{K}_{ln}(t'')\right],\\c_k(t)&=-i\int_0^t dt'\mathcal{K}_{kn}(t')+O(\mathcal{K}^2)\quad\text{for } k\neq n\ .\end{aligned}\tag{5}$$

Substituting this expression for c_n in (3), we can immediately read off the effective action produced by "integrating out" the fast variables, under the assumption that transitions among instantaneous states are neglected. The final result is

$$S_{\text{eff}}^{(n)}=\int\left[-E_n(\mathbf{Q})+\hbar\dot{\mathbf{Q}}\cdot\mathbf{A}^{(n)}+i\hbar\int_0^t dt'\sum_l\mathcal{K}_{nl}(t)\mathcal{K}_{ln}(t')\right]dt\ ,$$

where we have also neglected, to be justified later, contributions of order $\mathcal{K}^3$ to c_n.

The expression for $S_{\text{eff}}^{(n)}$ is non-local in time; but this can be considerably simplified if we are interested only in the leading contributions in $1/M$. Note that $\mathcal{K}$ is linear in $\dot{\mathbf{Q}}$ and that the last term in $S_{\text{eff}}^{(n)}$ contains the operator product $\mathcal{O}_{ab}\equiv T\dot{Q}_a(t)\dot{Q}_b(t')$ which admits an expansion in terms of local operators. This operator is not infrared divergent due to the two time derivatives. The leading contribution in the operator-product expansion is proportional to the identity operator, the coefficient being the expectation value of $\mathcal{O}$ in the "perturbative" vacuum of $\mathbf{Q}$; that is, the leading contribution in $1/M$ can be obtained by averaging $\mathcal{O}$ using the free action $S_0\equiv\frac{1}{2}M\int dt\,\dot{\mathbf{Q}}^2$. The final result is

$$\mathcal{O}_{ab}=\frac{i\hbar}{M}\delta(t-t')\delta_{ab}+\cdots\ ,$$

where the ellipsis indicates higher powers of $1/M$. As was to be expected, the leading term is proportional to a delta function: in the limit of large M only contact terms survive. Within this approach it is also clear that the neglected $O(\mathcal{K}^3)$ terms are of order $\hbar/M^2$ or higher. Note that we have assumed that V_0 is independent of M; if this condition is not met, the above results must be modified: for example, a quadratic term in V_0 which grows linearly with M would lead to a nonlocal contribution to the effective action of order $\hbar/M$.

The leading corrections to the above expression come from a quadratic term in V_0 and are of order $\hbar/M^{3/2}$; corrections produced by cubic or higher terms in V_0 are of order $\hbar/M^2$.

If the above expansion for $\mathcal{O}$ is substituted in $S_{\text{eff}}^{(n)}$ we get

$$S_{\text{eff}}^{(n)}=\int dt(\hbar\dot{\mathbf{Q}}\cdot\mathbf{A}^{(n)}-V_{\text{eff}}^{(n)}+\cdots)\ ,$$

which, when combined with the action for the slow coordinates, $\int(\dot{\mathbf{Q}}^2/2M-V_0)dt$, reproduces (1). Thus the usual adiabatic formulas are capable of reproducing the BO Hamiltonian $H_{\text{eff}}^{(n)}$. The procedure is not, however, straightforward as $H_{\text{eff}}^{(n)}$ contains terms of order $\hbar^2$, and these originate from the corrections to the usual adiabatic expressions. The final expansion is consistent since the neglected terms are of higher order in $1/M$.

These considerations do not address the corrections induced by the transitions among "fast" states as indicated by the nonzero c_k in (5). These terms must induce an imaginary term in $S_{\text{eff}}^{(n)}$; indeed, a nonzero c_k for $k\neq n$ indicates that, as time progresses, probability is drained from state $|n\rangle$ and distributed among all the states. Thus, from the point of view of state $|n\rangle$ alone, the evolution is nonunitary. This effect is in fact included in the imaginary contributions to $\mathcal{O}$, and therefore must be of order $\hbar/M^{3/2}$. But we can also see this explicitly: let

$$\theta\equiv\sum_{k\neq n}|c_k|^2\ ;$$

then we have $\theta+|c_n|^2=1$, and, therefore, $|c_n|=\sqrt{1-\theta}\simeq1-\theta/2\simeq\exp(-\theta/2)$. It follows that the imaginary term in $S_{\text{eff}}^{(n)}$ is $i\hbar\theta/2$; using (5) we obtain

$$\text{Im}S_{\text{eff}}^{(n)}\simeq\frac{\hbar}{2}\int dt\,dt'\sum_k\mathcal{K}_{nk}(t)\mathcal{K}_{kn}(t')\ ,$$

this expression contains the operator product $\mathcal{G}_{ab}\equiv\dot{Q}_a(t)\dot{Q}_b(t')$ (*without* the time ordering). The leading contribution (in $1/M$) to the operator-product expansion of $\mathcal{G}$ vanishes as $V_0\to0$, therefore $\theta\sim\hbar/M^{3/2}$.

From the above considerations we conclude that the effective action for the slow variables is given by $\int L_{\text{eff}}^{(n)}$, with $L_{\text{eff}}^{(n)}$ defined in (1); these results reproduce the formulas obtained by conventional methods. We have also seen that the BO approximation summarizes the leading terms in an expansion in $1/M$, which in general differs from an expansion in powers of $\hbar$. The corrections to $H_{\text{eff}}^{(n)}$ are of order $\hbar/M^{3/2}$, $\hbar/M^2$.

Though the above method is quite general, there are alternative procedures[4] which, in favorable cases, yield the corrections to the adiabatic approximation using symmetry principles. As a specific example assume we have a set of conserved quantities $\mathcal{J}^r=j^r(\mathbf{p},\mathbf{q})+J^r(\mathbf{P},\mathbf{Q})$ and that $H_f=H_f^{(0)}(\mathbf{p},\mathbf{q})+Q_aF_r^aj^r$. We also assume $[H_f^{(0)},j^r]=0$, $[H_s,J^r]=0$ and that the action of J^r on Q_a is of the form $i[J^r,Q_a]=\sum_bT_{ab}^rQ_b$.

If we define $C_{abc}\equiv\sum_rF_r^aT_{cb}^r$, then a straightforward application of the formalism developed in Ref. 4 yields

$$\frac{d}{dt}\frac{\delta S_{\text{eff}}^{(n)}}{\delta Q_a}=C_{abc}Q_b\frac{\delta S_{\text{eff}}^{(n)}}{\delta Q_c}\ .\tag{6}$$

Now we expand $S_{\text{eff}}^{(n)}=\int dt[W(\mathbf{Q})+A_a(\mathbf{Q})\dot{Q}_a+\cdots]$ which, when substituted in (6), requires

$$C_{abc}Q_b\frac{\partial W}{\partial Q_c}=0\ ,$$
$$C_{abc}Q_b\left[\frac{\partial A_d}{\partial Q_c}-\frac{\partial A_c}{\partial Q_d}\right]=\frac{\partial^2 W}{\partial Q_a\partial Q_d}\ . \tag{7}$$

These equations express the invariance of the theory under the transformations generated by the $\mathcal{J}$, and in some cases fully determine A once W is known. For example, if $\mathbf{Q}$ constitutes a three-dimensional vector, and $C_{abc}=\epsilon_{abc}$, then we must have $W=\lambda|\mathbf{Q}|+c$ (λ,c arbitrary constants), and A_a is the vector potential corresponding to an Abelian monopole of strength λ. In general (7) does not fully determine A, but it can be quite useful in restricting the possible form it can take. For further developments see Ref. 4.

For the BO approximation we assume that the C have no dependence on M and expand W and A in powers of $1/M$. Then the above constraints are solved iteratively (note that for consistency terms in two time derivatives must be considered together with those of order $1/M^2$). It must be kept in mind, however, that in general the form we used for H_f is not correct for many applications and that the equations must be modified accordingly.

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