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Citation: J. Chem. Phys. **107**, 10662 (1997); doi: 10.1063/1.474182
View online: http://dx.doi.org/10.1063/1.474182
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v107/i24
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Nonadiabatic effects in molecular adiabatic systems: Application to linear plus quadratic $E\otimes e$ system

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(Received 20 June 1997; accepted 2 September 1997)

In this publication I treat two subjects both connected to electronic nonadiabatic transitions. The first is related to the general single-state Born–Oppenheimer equation. Such an equation was recently derived by Baer and Englman [Chem. Phys. Lett. **265**, 105 (1997)]; here it is derived again in a different and more instructive way. The second is related to the ''linear plus quadratic $E\otimes e$ system''. For this system we derive the adiabatic–diabatic-transformation (ADT) angle [Chem. Phys. Lett. **35**, 112 (1975)] and show that it is identical to the phase factor obtained by Zwanziger and Grant [J. Chem. Phys. **87**, 2734 (1987)]. © *1997 American Institute of Physics.* [S0021-9606(97)00146-3]

I. INTRODUCTION

Degenerate states may be formed by a division of a Hamiltonian into two parts, a fast varying part and a slow varying part and therefore their effects are a general subject within quantum mechanics.[1–3] Electronic degeneracies within molecular physics is an old subject that goes back to the early days of quantum mechanics. It has its roots in the BO expansion[4] but then the vibronic coupling as discussed by Renner,[5] Teller,[6] Jahn–Teller,[7] and Longuet–Higgins (LH) and co-workers[8] (see several reviews on this subject[9–11]) indicated the potential impact of this phenomenon that goes also beyond molecular systems as we just mentioned above.[1–3] It is now well accepted that electronic degeneracies affect the spectra of isolated molecules[11] and more recently it was verified, theoretically numerically, that they are capable of affecting scattering processes.[12]

When considering the interaction of the electronic ground state with higher electronic states we encounter such concepts as nonadiabatic effect, degenerate state (e.g., conical intersection), phase (or phase factor),[8,13] adiabatic–diabatic-transformation (ADT) angle,[14] the molecular Aharonov–Bohm (MAB) effect,[15] and more recently, geometrical phase.[1] Some of these subjects were introduced as independent concepts unrelated to some of the others. In three recent publications we showed[12(a),16,17] that the phase factor has its roots in the nonadiabatic coupling terms and therefore the same applies to the geometrical phase.[17] The MAB effect was introduced as a concept associated with the phase factor.[15] In fact it is a much more general feature, associated with the nonadiabatic coupling terms, and it emerges from the BO expansion, as was shown by Pacher, Cederbaum, and Koppel[10] (see also Ref. 18). As was discussed by us in the past[12(a),14,16,17] and as I shall continue to do here in a different way and for different cases, all these concepts are related to each other and have the same origin, namely, the electronic nonadiabatic coupling terms.

The existence of electronic degenerate states and their potential importance for molecular systems was already recognized in the thirties by authors such as Renner,[5] Teller[6] etc.[7] but it was only in the late fifties and the early sixties that LH and co-workers[8,13] revealed that degenerate states may lead to nonunique (in the nuclear coordinates) electronic eigenfunctions. Moreover to correct for this deficiency they introduced a phase factor to modify the electronic eigenfunctions and make them unique without affecting their electronic character. Introducing the phase factor was the correct thing to do.

About two decades ago, while treating charge transfer processes during molecular collisions, the present author, considered the transformation from an adiabatic to a diabatic framework.[14] This transformation was carried out by an orthogonal matrix (assuming all electronic eigenfunctions are real), which was shown to be a solution of an integral equation which contains, as a kernel, the nonadiabatic coupling matrix. Within this study the two-state case was discussed as a special case resulted in a new angle, α-the ADT angle. This angle can be easily calculated for any number of coordinates (although in the first paper[14(a)] I discussed the two-coordinate case only). Recently I showed that the LH phase factor and the ADT angle, up to a constant, are identical[17] which implies that the LH phase is not just an *ad hoc* accidental mean to correct for symmetries but a legitimate magnitude that has its roots in the BO treatment.

In the present publication I shall address two closely connected subjects each of which stands on its on ground. In Sec. II I shall present a two-state model, derive from it the single-state equation in a different but more instructive way than in the previous derivation[16] and then present the formulae for the phase factor (which is identical to ADT angle) and the Berry phase.[17] However, it is important to emphasize that this new derivation is less general as it assumes the resolution of the unity in terms of two states, an assumption we managed to circumvent in the previous derivation.[16] In Sec. III I shall discuss the linear plus quadratic $E\otimes e$ system and show that the findings of Zwanziger and Grant (ZG)[19] are closely connected to the nonadiabatic coupling terms. A brief discussion and concluding remarks will be given in Sec. IV.

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II. THE TWO-STATE CASE

Our manifold is made up of two real electronic states $|\phi_1\rangle$; $i=1,2$ which are associated with two nuclear wave functions: χ_i; $i=1,2$ (which are not necessarily real). The following definitions are made:

$$|\phi\rangle=\frac{1}{\sqrt{2}}(|\phi_1\rangle+i|\phi_2\rangle) \tag{1}$$

and

$$\chi=\frac{1}{\sqrt{2}}(\chi_1-i\chi_2). \tag{2}$$

Presenting the total wave function Ψ in the form

$$|\Psi\rangle=\chi_1|\phi_1\rangle+\chi_2|\phi_2\rangle, \tag{3}$$

it can also be written as

$$|\Psi\rangle=\chi|\phi\rangle+\tilde{\chi}|\phi^*\rangle, \tag{4}$$

where $|\phi^*\rangle$ is the complex conjugate of $|\phi\rangle$ and $\tilde{\chi}$ is defined as

$$\tilde{\chi}=\frac{1}{\sqrt{2}}(\chi_1+i\chi_2). \tag{5}$$

It is important to remember that χ_i; $i=1,2$ are not necessarily real.

Next is introduced the electronic hamiltonian $\mathbf{H}_e$ for which $|\phi_i\rangle$; $i=1,2$ are assumed to be eigenfunctions

$$\mathbf{H}_e|\phi_i\rangle=u_i|\phi_i\rangle; \quad i=1,2. \tag{6}$$

Here u_i, $i=1,2$ are the electronic eigenvalues which parametrically depend on the nuclear coordinates. In what follows it is assumed that $u_2\geqslant u_1$ for any given nuclear configuration. Using Eq. (6) one can show

$$H_e|\phi\rangle=u_1|\phi\rangle+\tfrac{1}{2}(u_2-u_1)(|\phi\rangle-|\phi^*\rangle). \tag{7}$$

To continue I shall use the following relations (they all are straightforward outcomes of what was presented so far):

$$\langle\phi|\nabla^n\phi^*\rangle=0; \quad n=1,2, \tag{8}$$

$$\langle\phi|\nabla\phi\rangle=-i\tau_{12}, \tag{9}$$

where τ_{12} is the nonadiabatic coupling term defined as

$$\tau_{12}=\langle\phi_1|\nabla\phi_2\rangle \tag{10}$$

and

$$\langle\phi|\nabla^2\phi\rangle=-\tau_{12}^2+i\nabla\tau_{12}. \tag{11}$$

The symbol ∇ stands for the gradient

$$\nabla=\left(\frac{\partial}{\partial q_1},\frac{\partial}{\partial q_2}\cdots\frac{\partial}{\partial q_N}\right), \tag{12}$$

where $q_1,q_2,\ldots$ are a set of N (mass scaled) nuclear coordinates.

It is important to mention that Eqs. (10) and (11) follow from the fact that the identity can be resolved in terms of two states namely

$$\mathbf{I}=|\phi_1\rangle\langle\phi_1|+|\phi_2\rangle\langle\phi_2|. \tag{13}$$

Next are considered the total Hamiltonian $\mathbf{H}$ which will be written in the form

$$\mathbf{H}=\mathbf{H}_e+\mathbf{T}_n, \tag{14}$$

where $\mathbf{T}_n$ is the nuclear kinetic energy namely

$$\mathbf{T}_n=-\frac{1}{2m}\nabla^2, \tag{15}$$

and the full Schrödinger equation

$$(\mathbf{H}-E)\Psi=0, \tag{16}$$

where E is the total energy. Substituting Eq. (4) for Ψ, Eq. (14) for $\mathbf{H}$ and applying the various relations presented so far, yield for Eq. (16) the expression

$$\left(-\frac{1}{2m}\nabla^2+(u_1-E)\right)(\chi|\phi\rangle+\tilde{\chi}|\phi^*\rangle)$$
$$-\tfrac{1}{2}(u_2-u_1)(\chi-\tilde{\chi})(|\phi\rangle-|\phi^*\rangle)=0. \tag{17}$$

Multiplying Eq. (17) once by $\langle\phi|$ and once by $\langle\phi^*|$ and integrating over the electronic coordinates yields the following two coupled equations:

$$\left(-\frac{1}{2m}\nabla^2+(u_1-E)+\frac{1}{2m}(\tau_{12}^2-i\nabla\tau_{12})\right)\chi$$
$$-\frac{i}{m}\tau_{12}\cdot\nabla\chi+\frac{1}{2}(u_2-u_1)(\chi-\tilde{\chi})=0 \tag{18}$$

and

$$\left(-\frac{1}{2m}\nabla^2+(u_1-E)+\frac{1}{2m}(\tau_{12}^2+i\nabla\tau_{12})\right)\tilde{\chi}$$
$$+\frac{i}{m}\tau_{12}\cdot\nabla\tilde{\chi}+\tfrac{1}{2}(u_2-u_1)(\tilde{\chi}-\chi)=0. \tag{19}$$

It is noticed that Eq. (19) is the complex conjugate of Eq. (18) only in case both χ_i; $i=1,2$ are real. The interesting feature of the two coupled equations is that although we are within the adiabatic representation the coupling is essentially a potential coupling, but not as usual due to an off-diagonal matrix element but due to the difference between the two diagonal elements.

Equations (18) and (19) can be decoupled in case $E\ll u_2$ at every point in configuration space (this assumption is reminiscent of the adiabaticity requirement of Berry[1]). The reason being that in such a case the nuclear wave function $\chi_2(=(i\sqrt{2}(\tilde{\chi}-\chi))$ associated with the upper electronic state is negligible small at every point whereas the difference (u_2-u_1) is always finite. As a result the product between the two is negligible small and so the last term, in each of the two equations, can be discarded. Thus Eq. (18) becomes

$$\left(-\frac{1}{2m}\nabla^2+(u_1-E)+\frac{1}{2m}(\tau_{12}^2-i\nabla\tau_{12})\right)\chi$$
$$-\frac{i}{m}\tau_{12}\cdot\nabla\chi=0, \tag{20}$$

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and a similar equation is obtained for $\tilde{\chi}$. Equation (20) was derived by us before[16] in a somewhat different way but applying the same arguments.

The features of Eq. (20) for case that the nonadiabatic coupling term, τ_{12}, becomes singular at a point, was studied by us numerically[12(a),12(b)] and theoretically.[16,17] In particular we showed the connection between the phase factor (as well as the Berry phase) and the nonadiabatic coupling term.

In the next chapter we shall derive the expression of τ_{12} for the linear plus quadratic $E\otimes e$ system as well as the corresponding expressions for the phase factor and the Berry phase. Therefore, I shall next present for completeness without a proof, the formulae for both the phase factor and the Berry phase:

(a) If s_0 and s are two points on a path Γ in our N-dimensional space then the phase factor $\alpha(s)$ is given in the form[17]

$$\alpha(s)=\alpha(s_0)-\int_{s_0}^{s}\tau_{12}\cdot\mathbf{ds}, \tag{21a}$$

which due to Eq. (9) can also be written as

$$\alpha(s)=\alpha(s_0)-i\int_{s_0}^{s}\langle\phi|\nabla\phi\rangle\cdot\mathbf{ds}. \tag{21b}$$

Here the integral is carried out along Γ (a unique solution is guaranteed for the case that Curl $\tau_{12}=0$[14(a)]).

(b) The corresponding Berry phase γ along a closed loop C is given in the form

$$\gamma=-\oint_C\tau_{12}\cdot\mathbf{ds}, \tag{22a}$$

which due to Eq. (9) can also be written as

$$\gamma=-i\oint_C\langle\phi|\nabla\phi\rangle\cdot\mathbf{ds}. \tag{22b}$$

The expression, in Eq. (22b), we obtained for the Berry phase looks very similar to the expression written by Berry but is, in fact, different because $|\phi\rangle$ is not an eigenstate but is a linear combination of the first and the second eigenstates [see Eq. (1)]. Moreover although being not real it is not necessarily a single valued function of the nuclear coordinates.

This completes the representation for the two-surface case.

III. THE LINEAR PLUS QUADRATIC $E\otimes e$ SYSTEM: DERIVATION OF THE NONADIABATIC COUPLING TERM AND THE GEOMETRICAL PHASE

As is noticed from Eq. (20) the new terms that were added to the ordinary single-surface BO equation are all related to τ_{12}. The relevance and importance of τ_{12} was recently demonstrated in two numerical studies[12(a),12(b)] as well as in a theoretical study by BE who considered the linear $E\otimes e$ Jahn–Teller problem.[20] In the present publication the BE treatment is extended by adding to the electronic Hamiltonian a quadratic electronic-nuclear coupling term. This extended model was treated about a decade ago by ZG[19] and among other things ZG revealed the existence of four degenerate points and calculated the corresponding Berry phases. Here I shall derive the nonadiabatic coupling terms using Eq. (10) and, employing Eq. (22a), calculate the corresponding Berry phases. The reason for doing all that is to show that using our straightforward approach we derive identical analytic expressions for the corresponding magnitudes without the need to use complex algebra, explicitly requiring single valued eigenfunctions etc.

Let me consider the following electronic Hamiltonian:

$$\left\{-\frac{1}{2}E_{\mathrm{el}}\frac{\partial^2}{\partial\theta^2}-2k\rho\cos(2\theta-\varphi)-g\rho^2\cos 2(\theta-\varphi)-u(\rho\varphi)\right\}\phi(\theta|\rho\varphi)=0, \tag{23}$$

where θ is the electronic coordinate, ρ and φ are nuclear coordinates, ϕ is an electronic eigenfunction (namely either ϕ_1 and ϕ_2 from the previous chapter) and u is the corresponding eigenvalue, both depend parametrically on ρ and φ (it is noticed that the second and the third terms are the linear and the quadratic coupling terms, respectively). Choosing a solution of the form

$$\zeta=a\cos\theta+b\sin\theta, \tag{24}$$

leads to the following eigenvalue problem:

$$\begin{pmatrix}\frac{1}{2}E_{\mathrm{el}}+\frac{1}{2}U_1-u & \frac{1}{2}U_2\\ \frac{1}{2}U_2 & \frac{1}{2}E_{\mathrm{el}}-\frac{1}{2}U_1-u\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix}=\begin{pmatrix}0\\ 0\end{pmatrix}, \tag{25}$$

where U_i; $i=1,2$ are defined as

$$U_1=2k\rho\cos\varphi+g\rho^2\cos(2\varphi) \tag{26a}$$

and

$$U_2=2k\rho\sin\varphi-g\rho^2\sin(2\varphi). \tag{26b}$$

From Eq. (25) we get that the eigenvalues of the matrix are

$$u_{1,2}=E_{\mathrm{el}}\pm\rho\sqrt{k^2+\tfrac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi}, \tag{27}$$

and they are identical to those of ZG. As for the eigenfunctions we find that

$$\phi_1=-a\cos\theta+b\sin\theta, \tag{28a}$$

$$\phi_2=b\cos\theta+a\sin\theta \tag{28b}$$

where

$$a=\sqrt{\frac{G-U_1}{2\pi G}}\quad\text{and}\quad b=\sqrt{\frac{G+U_1}{2\pi G}}, \tag{29}$$

and G is

$$G=2\rho\sqrt{k^2+\tfrac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi}. \tag{30}$$

Having obtained the explicit expressions for ϕ_i; $i=1,2$ we are in position to derive the two components of τ_{12}, namely, $\tau_{12\rho}$ and $\tau_{12\varphi}$. Thus

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$$\tau_{12\varphi}=\frac{1}{\rho}\left\langle \phi_1\left|\frac{\partial}{\partial\varphi}\phi_2\right.\right\rangle$$
$$=\frac{1}{2\rho}\frac{k^2-\frac{1}{2}(g\rho)^2-\frac{1}{2}kg\rho\cos 3\varphi}{k^2+\frac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi} \tag{31a}$$

and

$$\tau_{12\rho}=\left\langle \phi_1\left|\frac{\partial}{\partial\rho}\phi_2\right.\right\rangle=-\frac{1}{4}\frac{kg\sin 3\varphi}{k^2+\frac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi}. \tag{31b}$$

It is noticed that $\tau_{12\varphi}$ is singular at four points (as was also revealed by ZG) namely at $\rho=0$, and at $\rho=(2k/g)$ and $\varphi=\pi/3$, π, and $5\pi/3$. As for $\tau_{12\rho}$ it does not seem to have singular points; at $\rho=0$ it is regular and at the other three points it is not well defined.

Once the components of τ_{12} are obtained we can calculate the phase factor $\alpha(s)$ employing Eq. (21a), namely

$$\alpha(\rho,\varphi)=\alpha(\rho_0,\varphi_0)-\int_{\varphi_0}^{\varphi}\tau_{12\varphi}(\rho,\varphi)\rho\mathbf{d}\varphi$$
$$-\int_{\rho_0}^{\rho}\tau_{12\rho}(\rho,\varphi_0)\mathbf{d}\rho. \tag{21b}$$

Before deriving $\alpha(\rho,\varphi)$ I shall prove, that for this system, $\alpha(\rho,\varphi)$ is independent of the particular path between (ρ,φ) and (ρ_0,φ_0). The necessary condition for this to happen, as was mentioned earlier, is that Curl $\tau_{12}=0$[14(a),14(b)] which means that the two components of τ_{12} have to fulfill the condition

$$\frac{\partial\tau_{12\rho}}{\partial\varphi}=\frac{\partial(\rho\tau_{12\varphi})}{\partial\rho}, \tag{32a}$$

which they do because the two expressions are equal to

$$\frac{\partial\tau_{12\rho}}{\partial\varphi}=\frac{\partial(\rho\tau_{12\varphi})}{\partial\rho}$$
$$=-\frac{3kg}{4}\frac{kg\rho+(k^2+\frac{1}{4}g^2\rho^2)\cos 3\varphi}{k^2+\frac{1}{4}g^2\rho^2+kg\rho\cos 3\varphi}. \tag{32b}$$

Now, to derive $\alpha(\rho,\varphi)$ Eqs. (31) are substituted in Eq. (21b) thus yielding

$$\alpha(\rho,\varphi)=\alpha(\rho,\varphi_0)$$
$$-\frac{1}{2}\int_{\varphi_0}^{\varphi}\frac{k^2-\frac{1}{2}(g\rho)^2-\frac{1}{2}kg\rho\cos 3\varphi}{k^2+\frac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi}d\varphi, \tag{33a}$$

where $\alpha(\rho,\varphi_0)$ is given in the form

$$\alpha(\rho,\varphi_0)=\alpha(\rho_0,\varphi_0)-\frac{kg\sin 3\varphi_0}{4}$$
$$\times\int_{\rho_0}^{\rho}\frac{1}{k^2+\frac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi_0}d\rho. \tag{33b}$$

[Ordered line integrals, in this context, are discussed in Ref. 14(c)] The expression for $\alpha(\rho,\varphi)$ can be simplified by choosing $\varphi_0=0$ so that $\alpha(\rho,\varphi)$ is given by Eq. (33a) only. Now, since the integrand of Eq. (33a) has poles at the above mentioned four points (namely at $\rho=0$, and at $\rho=(2k/g)$ and $\varphi=\pi/3$, π, and $5\pi/3$) the value of α is defined up to multiples of π.[19] The same holds for the Berry phase, γ, which becomes equal to α when calculated for a closed loop [see Eq. (22a)]. The value of γ is determined by the number of poles a given loop encloses. For instance if ρ is chosen so that $\rho<(2k/g)$ a Berry phase is obtained by performing the integral in Eq. (32a) within the two limits $(0,2\pi)$ only, namely

$$\gamma=-\frac{1}{2}\int_0^{2\pi}\frac{k^2-\frac{1}{2}(g\rho)^2-\frac{1}{2}kg\rho\cos 3\varphi}{k^2+\frac{1}{4}(g\rho)^2+kg\rho\cos 3\varphi}d\varphi. \tag{34}$$

The value of this integral can be calculated using formulae of Gradsteyn and Ryzhik[21] (see also Ref. 19) and as long as $\rho<(2k/g)$, γ is equal to

$$\gamma=-\pi. \tag{35}$$

The analysis for the more general cases was carried out by ZG and applies to our presentation as well because their integrands are identical to those of ours. The only difference is that in their case the value of power ''s'' (in their notation) can be any half odd integer and in our case it is equal to 1/2 (in our case this is not an assumption, it simply emerges from the theory).

For completeness I will also briefly refer to the two extreme cases namely when either g or k are equal to zero. For the first case $(g=0)$ known as the Jahn–Teller case[9(b)] we see that α becomes: $\alpha=-\varphi/2$[20] which leads to a Berry phase that is equal to $\gamma=-\pi$. The second case where $k=0$ known as the Renner–Teller case we get for α that $\alpha=-\varphi$ which leads to a Berry phase that is equal to $\gamma=-2\pi$.

IV. CONCLUSIONS

In this publication we considered two subjects associated with the intimate relations between the nonadiabatic coupling terms and phase factors and Berry phases.

First we derived the extended single-state BO equation in a somewhat different way (as compared to the previous one[16]) and then presented (without proof) the expressions for the above mentioned phases. The new way of deriving the extended single-state BO equation is more instructive (and eventually also more common) but its validity is less general as it demands the resolution of the unity in terms of two states only. In our previous derivation[16] this assumption was avoided. There, instead, we only demanded that the electronic nonadiabatic coupling terms between states in the two-state manifold and states belonging to the ''rest of world'' be small.

Although it was to a certain extent a repetition of derivations done in the past, we encountered a new expression, namely, Eq. (9) which later led to a (conceptually) new representation of the phase factor [see Eq. (21b)] and the Berry

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phase [see Eq. (22b)]. We argued many times in the past that the LH phase and the ADT angle are identical and that the Berry phase ''which is given by a circuit integral in parameter space'' (namely, in the nuclear configuration space) over $\langle n|\nabla n\rangle$ where $|n\rangle$ is a single-valued eigenfunction can be shown to be a circuit integral over the nonadiabatic coupling term τ_{12}. In the present work we showed, for the first time, that τ_{12} is equal to $i\langle\phi|\nabla\phi\rangle$, and therefore the Berry phase is given by a circuit integral over $\langle\phi|\nabla\phi\rangle$ multiplied by i where $|\phi\rangle$ is not a pure eigenfunction and not a necessarily single-valued function. This is to a certain extent an unexpected result but, then there are several indications in the literature as to its validity. Aharonov *et al.*[22] recently showed ''that Berry phase which is relevant to the case of no level mixing, can be generated by an A which does nothing but mix levels.'' A in this case is identical to $i\tau_{12}$. In another publication Aharonov and Anandan[23] showed that Berry's phase is a magnitude which depends only on the (closed) path in configuration space, regardless of whether or not the circuit is traversed slowly enough for the adiabatic approximation to be fulfilled. As can be seen our derivation of the Berry phase did not make use of this approximation and therefore it is related to Aharonov and Anandan findings as well.

In several publications[12(a),12(b),16,17] we pursued the idea that the ADT angle and the phase factor are identical. In a recent publication[17] I even proved it, mathematically, step-by-step for the adiabatic case. This means that the phase factor introduced by LH to correct for the nonsingle-valuedness of the electronic wave functions is, in fact, a magnitude of a much more fundamental importance which has its roots in the BO expansion. In a recent publication BE[20] showed that the ADT angle and the phase factor are identical for the Jahn–Teller case. Here the fact that the two are identical is proved for a much more general case, namely, the linear plus quadratic $E\otimes e$ system. I showed that applying our general recipe for calculating the ADT angle yields the phase factors (and, following that, also the Berry phases) without the necessity of introducing various *ad hoc* assumptions as was done by ZG. This brings me to the last subject in this publication: ZG, in their study, *distinguished* between the ''manifestation of the geometrical phase'' and ''the effects of the nonadiabatic processes.'' In other words they implied that there is no relation, between the nonadiabatic coupling terms and the Berry phase. In the present study, like in the two previous studies, the two are proven to be related; moreover a necessary (not sufficient) condition for a Berry phase to exist is having singular nonadiabatic coupling terms.

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