JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 16 22 OCTOBER 2002

Born–Oppenheimer invariants along nuclear configuration paths

Roi Baer[a)]
Department of Physical Chemistry and the Lise Meitner Minerva Center for Quantum Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Received 3 April 2002; accepted 29 August 2002)

Whenever a quantum chemist extracts the eigenstate of an electronic Hamiltonian, he makes, consciously or not, a decision concerning the phase of the wave function. This is done for each calculated state at each nuclear position. Thus he defines a Born–Oppenheimer (BO) frame of reference. There is no absolute phase just as there is no absolute position or time in mechanics. This leads naturally to the question: What are the quantities which do not depend on the arbitrary phases, i.e., what are the BO invariants? In this article we identify BO invariants with respect to an arbitrary path in nuclear configuration space. We identify invariant electronic states along these paths and their Aharonov–Anandan geometric phases. For closed loops not passing through electronic energy degeneracies these invariant states are the BO adiabatic wave functions and the phases are the Berry phases. The results establish rigorous relations between the full nonadiabatic couplings matrix and the geometric phases. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1515768]

I. INTRODUCTION

Molecules are composed of light electrons and heavy nuclei. Exploiting this fact, by adopting a quantum mechanical basis, which simplifies when nuclei are frozen, is called the Born–Oppenheimer (BO) picture.[1] It introduces two basic concepts: the adiabatic (also called BO) potential surfaces and the nonadiabatic couplings (NACs). The BO *approximation* assumes that the NACs are negligible.[2] This greatly simplifies the mathematical treatment of molecular wave functions and results in the appealing picture depicting molecular dynamics as the motion of nuclei under a potential. The BO approximation is frequently accurate enough to allow the detailed understanding and prediction of molecular properties and processes.

For a large class of chemically interesting processes, the usual BO approximation, leads however to gross qualitative errors. These are typically classified as *nonadiabatic processes* and include for example, most of the photochemical reactions in nature. Here one must consider the effects of several electronic states so nonadiabatic couplings and sometimes several adiabatic surfaces must be addressed.

Several interesting discoveries made over the years concerning the BO picture had important ramifications on the application of nonadiabatic dynamics. Longuet–Higgins[3] revealed an interesting property of the BO picture: When a real adiabatic function is moved continuously around a conical intersection it changes sign upon returning to the initial position. The single-valuedness was restored by making the electronic wave function complex including a nuclear-dependent phase factor. These findings were not just curiosities, they have a profound effect on nuclear dynamics, as was first pointed out by Mead and Truhlar.[4,5] The work of Berry[6] and later Aharonov and Anandan[7] concerning cyclic evolution of the Hamiltonian and wave functions revealed the underlying structure and the generality of this phenomenon. The actual effects of Berry phases on chemical molecular processes are described and debated in recent literature.[8–20]

This article aims to establish the connection between the frequently used NACs and the geometric invariant phases. Starting from a basic practical observation concerning the behavior of the NACs along an arbitrary path in nuclear configuration space, we find a set of electronic states which have simple path–transport properties (Sec. II). These states are then associated to invariant phases which are subsequently connected to the Aharonov–Anandan theory.[7] In the case of loops that do not pass through electronic degeneracies these states are the adiabatic states and the phases are the Berry phases[6] (Sec. III). After examining an example (Sec. IV), involving a nonreal Hamiltonian we finalize by a short discussion of the possible implications these results have on truncating the Born–Oppenheimer approximation (Sec. V).

II. BORN–OPPENHEIMER PATH INVARIANTS

Suppose a quantum chemist calculates the eigenstates $\psi_n[s]$ and eigenenergies $\varepsilon_n[s]$ of the electronic Hamiltonian $H_e[s]$ of a given molecule. This calculation is repeated for all nuclear configurations along a path in nuclear configuration space $R(s)$ parametrized by a real number s. (Later, we will argue that our results are independent of parametrization.) He is careful to select the eigenstates in such a way that they are differentiable with respect to s, thus the adiabatic wave functions at $s+ds$ can be written as

$$\psi_n[s+ds]=\psi_n[s]+\dot{\psi}_n[s]ds, \tag{2.1}$$

where $\dot{\psi}_n=d\psi_n/ds$. The wave functions so defined depend only on the points of the path and not on the parametrization used. This is seen when one considers a different parametrization $R'(t)$ and $\phi_n[t]$. Defining $t(s)$ by the conditions

---

[a)] Electronic mail: roi.baer@huji.ac.ile; Fax: +972-2-651-3742.

$R(s)=R'(t(s))$ and demanding $\phi_n[t(s)]=\psi_n[s]$, Eq. (2.1) keeps its form $\phi_n[t+dt]=\phi_n[t]+\dot{\phi}_n[t]dt$ due to the chain rule of differentiation.

Now, suppose the total number of states being treated by the quantum chemist is such that the group of states at s span essentially the same space as that at $s+ds$ (for all s). Then,

$$\psi_n[s+ds]=\sum_m (\delta_{nm}+\tau_{nm}(s)ds)\psi_m[s], \tag{2.2}$$

where $\tau_{nm}(s)$ is the matrix of nonadiabatic couplings (NACs):

$$\tau_{nm}(s)=\langle\psi_m|\dot{\psi}_n\rangle. \tag{2.3}$$

(Note: in many texts this is defined as the *transpose* τ^T). It is intuitively clear that Eq. (2.2) is valid when all possible adiabatic states are included, but this condition can be relaxed when the NACs matrices $\tau_{nm}(s)$ decompose to blocks along the path.[21]

Using Eq. (2.2), we can write in general a *displacement* of the basis at s_0 to s:

$$\psi_n[s]=\sum_m D(s,s_0)_{nm}\psi_m[s_0], \tag{2.4}$$

where the numerical matrix D is defined by[22]

$$D(s,s_0)=\hat{P}\exp\left[\int_{s_0}^{s}\tau(s')ds'\right], \tag{2.5}$$

where $\hat{P}$ is the ordering symbol. We call this operation "displacement under D."

Now, consider a *second quantum chemist*, calculating adiabatic states and energies of the same Hamiltonian $H_e[s]$ along the same path. Of course, he obtains the same set of energies $\varepsilon_n[s]$ but each of the states he calculates can differ by a phase factor from those of the first chemist:

$$\tilde{\psi}_n[s]=e^{i\theta_n(s)}\psi_n[s]. \tag{2.6}$$

The second quantum chemist, being no better or worse than the first, will thus produce a different set of NACs. The relation between the two sets is

$$\tilde{\tau}_{nm}=e^{i(\theta_n(s)-\theta_m(s))}\tau_{nm}+i\dot{\theta}_n(s)\delta_{nm}. \tag{2.7}$$

This is quite a simple relation: The diagonal element $\tilde{\tau}_{nn}$ is boosted with respect to τ_{nn} by $i\dot{\theta}_n(s)$ while the nondiagonal elements of $\tilde{\tau}$ acquire a phase with respect to those of τ. Thus the *magnitude* of the nondiagonal elements remains unchanged, but their s-dependent phase does.

Plugging Eq. (2.6) into Eq. (2.4), it is clear by inspection that the relation between the D and $\tilde{D}$ matrices of the two quantum chemists is

$$\tilde{D}(s,s_0)=e^{i\theta(s)}D(s,s_0)e^{-i\theta(s_0)}, \tag{2.8}$$

where $\theta(s)$ is the *diagonal matrix with* $\theta_n(s)$ appearing on its diagonal.

The mere phase difference between the two sets of adiabatic wave functions used forces the quantum chemists to disagree about various quantities, for example, the τ's are different. If the dynamics of the molecule is to be determined solely in terms of the adiabatic surfaces and NACs, without any direct reference to the adiabatic electronic wave functions, then only invariant quantities are of importance.

In a slightly more technical jargon, we call the different possible phase choices "gauges." Equation (2.7) then is the gauge transformation of the NACs τ, while Eq. (2.8) is that of the D matrix. We search for gauge invariant quantities because these are expected to be intimately connected to physically measurable quantities of the molecule which cannot depend on specific choice of phase in the electronic wave function.

In order to identify such gauge invariant quantities, we first rewrite Eq. (2.8) as

$$\tilde{D}(s,s_0)=e^{i\theta(s_0)}[e^{i[\theta(s)-\theta(s_0)]}D(s,s_0)]e^{-i\theta(s_0)}. \tag{2.9}$$

Notice that from Eq. (2.7), $\theta(s)-\theta(s_0)=i\int_{s_0}^{s}\text{diag}[\tau(s')-\tilde{\tau}(s')]ds'$. Thus we can write the "rephased" transformation matrix:

$$C(s,s_0)=e^{-\int_{s_0}^{s}\text{diag}(\tau|s|)ds}D(s,s_0) \tag{2.10}$$

which, like $D(s,s_0)$, displaces the adiabatic states at s_0 to adiabatic states at s (the additional factor is a mere phase factor) but on C, the gauge transform is reduced to a s-independent unitary transformation:

$$\tilde{C}(s,s_0)=e^{i\theta(s_0)}C(s,s_0)e^{-i\theta(s_0)}. \tag{2.11}$$

What is the meaning of this? For one thing, this shows that the eigenvalues of the unitary matrix C, the phase factor $e^{i\beta_n}$ are invariant. That is, no matter which of the quantum chemists are asked, the phase factors they report for C are the same.

Notice that a displacement of an adiabatic state under C is an adiabatic state along the path:

$$\psi_n^{(C)}[s]=\sum_m C(s,s_0)_{nm}\psi_m[s_0]. \tag{2.12}$$

So what is special about $\psi_n^{(C)}[s]$? Thanks to Eq. (2.11), both chemists, following the same sequence of steps (but with their different NACs) will get the same set of adiabatic functions, apart of the *constant* phase factor $e^{i\theta_n(s_0)}$:

$$\tilde{\psi}_n^{(C)}[s]=e^{i\theta_n(s_0)}\psi_n^{(C)}[s]. \tag{2.13}$$

So this basis is in this sense *canonical*.

In general, the wave functions $\psi_n^{(C)}[s]$ are different from $\psi_m[s_0]$. However, certain linear combinations return at s to their values at s_0, apart from a phase factor. To see these, consider a column vector U with $U^T=(u_1 \quad u_2 \quad \dots)$ that defines a linear combination of wave functions: $\varphi_U[s_0]=\Sigma_m u_m\psi_m[s_0]$. In general, if C displaces $\psi_n[s_0]$ according to Eq. (2.12), this carriers over to any linear combination. Thus:

$$\varphi_U[s]=\sum_{m,n} u_m C(s,s_0)_{mn}\psi_n[s_0]. \tag{2.14}$$

Now, consider the case where $U=U_k$ is the left eigenvector of $C(s,s_0)$ belonging to the eigenvalue $e^{i\beta_k}$. Then Eq. (2.14) becomes

$$\varphi_{U_k}[s]=e^{i\beta_k(s)}\varphi_{U_k}[s_0] \tag{2.15}$$

which shows that $\varphi_{U_k}[s]$ is displaced by C to itself (apart from a phase) when the nuclei follow the path $s_0 \to s$.

The states $\varphi_{U_{k(s)}}$ form a closed path in projective space $\wp$. These paths have the meaning that their Aharonov–Anandan (AA) phase[7] is the invariant BO phase of the nuclear path.

We see how *any nuclear path*, not necessarily closed, generates a set of invariant loops in projective space, each loop having a geometrical AA phase factor $e^{i\beta_n}$ which is by our construction also a BO invariant. These results are independent of the path parametrization variable s. This follows from the use of line integrals.

III. LOOPS: RELATION TO BERRY'S PHASE

Up to now the path $R(s)$ was completely general. For closed paths, or loops, where there exists s_f, such that $R(s_0)=R(s_f)$, there are additional simplifications. Once the loop is closed, the adiabatic wave functions must return to themselves with at most a phase factor (we assume that there is no degeneracy along the path). Thus, the closed loop D matrix, which we denote as $D_\odot$ must be diagonal, and because it is unitary, the diagonal elements are pure phase factors: $e^{i\alpha_n}$.[21,23] These phases tell us something about the behavior of the adiabatic wave function once the loop is closed. For example, in the Longuet–Higgins model the wave function changes sign after transversal of a closed loop, thus the phase appearing $D_\odot$ is $\alpha_n=\pi$. However, due to the gauge freedom, the phase of $D_\odot$ is not an invariant. Instead, what Eq. (2.10) tells us that it is the phase of $C_\odot$ which is a loop invariant, given by:

$$\beta_n=\alpha_n+i\int_{s_0}^{s_l}\tau_{nn}(s)\,ds. \tag{3.1}$$

For closed loops the adiabatic functions themselves form the invariant loops in the projective space. This means that for loops, as discussed by AA and others,[24,25] β_n is the Berry phase.[6] We emphasize, that while the entire electronic basis is needed to prove Eq. (3.1), the final result is valid for each of the electronic states separately. This is in fact a formal proof of Berry's results, which assumed adiabatic evolution.

IV. EXAMPLE: COMPLEX CONICAL INTERSECTION

We test the general results in the case of conical intersection in the presence of spin–orbit coupling.[26] Using the model of Stone,[27] involving a Hermitian–Hamiltonian:

$$H_e=R\begin{pmatrix}\cos\theta & ie^{i\phi}\sin\theta\\ -ie^{-i\phi}\sin\theta & -\cos\theta\end{pmatrix}. \tag{4.1}$$

Diagonalizing H_e leads to the transformation:

$$A(\theta,\phi)=\begin{pmatrix}e^{i\phi/2}\cos\theta/2 & -ie^{i\phi/2}\sin\theta/2\\ -ie^{-i\phi/2}\sin\theta/2 & e^{-i\phi/2}\cos\theta/2\end{pmatrix}. \tag{4.2}$$

The columns of the matrix A are eigenvectors of the Hamiltonian. They depend on two nuclear parameters. Consider a circular precession, similar to Matsika *et al.*[26] around the U axis: $R=q$ and $\theta=\theta_0$ are frozen while ϕ revolves from 0 to 2π. The τ matrix [Eq. (2.3)] is constant:

$$\tau(\phi)=\frac{i}{2}\begin{pmatrix}\cos\theta_0 & -i\sin\theta_0\\ i\sin\theta_0 & -\cos\theta_0\end{pmatrix}. \tag{4.3}$$

The D-matrix [Eq. (2.5)] is: $D_\odot=-I$. So the wave functions change sign around the loop [seen also directly in Eq. (4.2)]. The invariant phases are calculated from Eq. (3.1) $\beta=\pi(1\mp\cos\theta_0)$. Conforming to the Berry theorem[6] relating the phase to the solid angle subtended by the loop. A different choice of wave function phase will not change the invariant phases, for example, multiplying Eq. (4.2) by $e^{i\phi/2}$, leads to a new NACs $\tilde{\tau}=i/2+\tau$, while the D-matrix equals the unit matrix ($\alpha_n=2\pi$), giving the same invariant phases.

V. DISCUSSION

We have focused in this article on the loop matrices $D_\odot$ and $C_\odot$. We have shown that for loops not going through electronic energy degeneracies these matrices have very simple structure: they are diagonal and contain only phase factors. The phase factors of the D-matrix describe the single-valuedness of the adiabatic states[22] and those of the $C_\odot$ involve the invariant phase factors, obtained from the Berry phases.

The essence of the BO approach is to represent a molecular process as an effective dynamics of just the nuclei in a small number of adiabatic states. Accordingly, the NAC matrices are truncated. However using a truncated set of NACs will destroy the gauge invariant phase associated with each path. In the case of a single conical intersection, this is avoided using a vector potential[4,11,12,28] or suitable representations.[9] For a multisurface case, it is essential to develop methods that keep as much of the invariant properties intact.[28–30]

ACKNOWLEDGMENT

This research was funded by the United States–Israel Binational Science Foundation (BSF) Grant No. 9800108, Jerusalem, Israel. The author thanks M. Baer for his encouragement of my work on this topic.

[1] M. Born and K. Huang, in *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).
[2] M. Born and J. R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).
[3] H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, Proc. R. Soc. London, Ser. A **244**, 1 (1958).
[4] C. A. Mead, Chem. Phys. **49**, 23 (1980).
[5] C. A. Mead and D. G. Truhlar, J. Chem. Phys. **70**, 2284 (1979).
[6] M. V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984).
[7] Y. Aharonov and J. Anandan, Phys. Rev. Lett. **58**, 1593 (1987).
[8] B. Lepetit and A. Kuppermann, Chem. Phys. Lett. **166**, 581 (1990).
[9] A. Kuppermann and Y. S. M. Wu, Chem. Phys. Lett. **205**, 577 (1993).
[10] D. W. Schwenke, S. L. Mielke, G. J. Tawa, R. S. Friedman, P. Halvick, and D. G. Truhlar, Chem. Phys. Lett. **203**, 565 (1993).
[11] X. D. Wu, R. E. Wyatt, and M. Dmello, J. Chem. Phys. **101**, 2953 (1994).
[12] R. Baer, D. M. Charutz, R. Kosloff, and M. Baer, J. Chem. Phys. **105**, 9141 (1996).
[13] D. R. Yarkony, Rev. Mod. Phys. **68**, 985 (1996).
[14] R. Englman, A. Yahalom, and M. Baer, Eur. Phys. J. D **8**, 1 (2000).
[15] M. Baer, J. Phys. Chem. A **105**, 2198 (2001).
[16] S. Mahapatra, H. Koppel, and L. S. Cederbaum, J. Phys. Chem. A **105**, 2321 (2001).
[17] D. R. Yarkony, J. Phys. Chem. A **105**, 6277 (2001).
[18] H. Muller, H. Koppel, and L. S. Cederbaum, J. Chem. Phys. **101**, 10263 (1994).

[19] T. Pacher, C. A. Mead, L. S. Cederbaum, and H. Koppel, J. Chem. Phys. **91**, 7057 (1989).
[20] S. Klein, M. J. Bearpark, B. R. Smith, M. A. Robb, M. Olivucci, and F. Bernardi, Chem. Phys. Lett. **292**, 259 (1998).
[21] M. Baer, Phys. Rep. **358**, 75 (2002).
[22] M. Baer, J. Phys. Chem. A **104**, 3181 (2000).
[23] M. Baer, Chem. Phys. Lett. **322**, 520 (2000).
[24] C. A. Mead, Rev. Mod. Phys. **64**, 51 (1992).
[25] J. W. Zwanziger, M. Koenig, and A. Pines, Annu. Rev. Phys. Chem. **41**, 601 (1990).
[26] S. Matsika and D. R. Yarkony, J. Chem. Phys. **116**, 2825 (2002).
[27] A. J. Stone, Proc. R. Soc. London, Ser. A **351**, 141 (1976).
[28] R. Abrol and A. Kuppermann, J. Chem. Phys. **116**, 1035 (2002).
[29] C. A. Mead and D. G. Truhlar, J. Chem. Phys. **77**, 6090 (1982).
[30] R. G. Sadygov and D. R. Yarkony, J. Chem. Phys. **109**, 20 (1998).