PHYSICAL REVIEW A **68**, 032501 (2003)

Relative likelihood of encountering conical intersections and avoided intersections on the potential energy surfaces of polyatomic molecules

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(Received 16 April 2003; published 3 September 2003)

We prove that conical intersections are much more likely than local minima of the electronic energy gap. Therefore, if one encounters a very small electronic energy gap along a path through configuration space, it is much more likely to be associated with the neighborhood of a conical intersection than with an avoided intersection.

DOI: 10.1103/PhysRevA.68.032501 PACS number(s): 31.50.Gh, 33.15.−e, 33.20.Lg, 34.20.Mq

I. INTRODUCTION

Our understanding of molecular phenomena is sometimes based on sharp selection rules and theorems, such as the noncrossing rule, the conservation of total angular momentum and parity, the Jahn-Teller theorem, and the nonexistence of strictly diabatic electronic states. More often, though, it is guided by fuzzier principles such as the Franck-Condon principle or the tendency of energy transfer processes to minimize changes in translational energy and spin quantum numbers. Complicated phenomena such as electrically nonadiabatic processes are especially in need of guiding principles, even fuzzy ones.

One way to establish such principles is by expanding a coupling term in powers of a small parameter. Using this approach, Born and Oppenheimer showed that the coupling of adiabatic electronic wave functions by nuclear kinetic energy is usually small [1]. More recently, using the same approach, it was shown that, although one cannot in general find strictly diabatic electronic states (states for which the coupling due to nuclear momentum and kinetic energy vanishes in any finite region), one can find electronic representations that reduce the coupling everywhere to a level of the same order as the nonadiabatic coupling of adiabatic states in regions where the Born-Oppenheimer principle is valid [2]. This principle gives useful guidance in the development of algorithms for calculating quasidiabatic states [3].

In the present article, we propose and prove another such principle, one that should prove useful in computations of coupled potential energy surfaces. In particular, we prove the following theorem. Let

$$G \equiv U_2 - U_1, \tag{1}$$

where U_1 and U_2 are adiabatic electronic energy levels, with U_2 the higher level by convention, so that G is never negative. Suppose that one calculates U_1 and U_2 along a path and encounters what looks like an avoided crossing, that is, G exhibits a local minimum where it has a very small value in atomic units. In this article, we show that, almost always, this will be because one has passed near a conical intersection, rather than a true avoided crossing corresponding to a true minimum in the gap G.

II. THEORY

Assume that one has found a point at which the gap G between two electronic states has the very low value ε, i.e., $\varepsilon \ll 1$. (Note: all quantities are in atomic units, where the unit of energy is the hartree, 27.2 eV.) The question we have posed is the following: Is it more likely that the point is closer to a conical intersection (CI) or to a minimum (min)? Clearly, the probability of each will be proportional to the volume of nuclear configuration space that has $G \leqslant \varepsilon$ due to each effect.

Let the dimension of the space be $d = 3n - 6$, where n is the number of atoms (assumed to be greater than or equal to 3). Consider a region of dimension L in all directions, with volume $V = L^d$. For a CI, we must have two conditions satisfied, $u = v = 0$.[4,5] If u and v are chosen as two of the coordinates in the neighborhood of the CI, then we will have $G \leqslant \varepsilon$ for a distance ε in the u and v directions (since G varies linearly with u and v), independent of the other $(d-2)$ coordinates, so the volume is $V(\mathrm{CI}) = L^{d-2}\varepsilon^2$.

A minimum of G requires that all components of grad G vanish, and this amounts to d conditions, so we will have minima only at isolated points. We also note that G varies quadratically in the distance from a minimum, so the volume is $V(\min) = \varepsilon^{d/2}$. Furthermore, only a fraction ε of the minima will have the anomalously low value ε of the gap, as addressed in the next paragraph.

Next consider the question of how many CI and minima there are. Assuming a density ρ for the zeros of a typical electronic matrix element in the problem, the number $N(\mathrm{CI})$ of CI's in the region is on the order of $\rho^2 L^2$. Similarly, the number $N(\min)$ of minima is $\rho^d L^d$. But most minima will have gaps larger than ε. Only a fraction ε of them will have the anomalously low value. So the number of minima of interest to us is $N(\min) = \varepsilon \rho^d L^d$.

We can now estimate the order of magnitude of the total volumes (V_{tot}) in the two cases. We obtain

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$$V_{\text{tot}}(\text{CI}) = N(\text{CI})V(\text{CI}) = \rho^2 L^d \varepsilon^2 \tag{2}$$

and

$$V_{\text{tot}}(\min) = N(\min)V(\min) = \rho^d L^d \varepsilon^{(d+2)/2}. \tag{3}$$

The ratio is

$$V_{\text{tot}}(\min)/V_{\text{tot}}(\text{CI}) = (\rho^2 \varepsilon)^{(d-2)/2}. \tag{4}$$

Recall that ε is small by definition, and d is at least 3, since $n \geqslant 3$ by definition of the problem under consideration. Next, we consider ρ. The density of zeros of the electronic matrix elements should be of the order of the density of zeros of the orbitals in the valence region, and this density is $O(1)$ in atomic units because the spacing (in bohrs) between nodes is $O(1)$. Therefore the ratio in Eq. (4) is a normally small number, and it rapidly becomes smaller as the size of the system (number of atoms n) becomes large, and as ε becomes small.

It follows that the principle is true: Almost always, if, along a path, there occurs a minimum ε in the electronic energy gap G, and it is much less than 1 hartree, then the minimum is near a CI. Exceptions can occur only if ρ becomes very large, or if the density of zeros is much larger for the components of grad G than for u and v, which are unlikely scenarios since these densities do not depend on any large or small parameter. Even in these cases, the probability of having discovered an exception becomes small as ε becomes small. This principle is similar in rigor to the Born-Oppenheimer principle; it follows from general considerations about the magnitudes of matrix elements and does not require a specific calculation of the matrix elements for each molecular system.

We note that spin-orbit coupling is neglected in the present treatment. Including spin-orbit coupling would have no effect on the discussion for a system with an even number of electrons (in the absence of external fields), but for an odd number of electrons, spin-orbit coupling lowers the dimensionality of the intersection.

III. DISCUSSION

The theorem we have just proved is a corollary of sorts to another fuzzy theorem, namely, conical intersections are not rare. That theorem seems ‘‘obvious’’ from a certain point of view,[6,7] but the literature now contains expressions of surprise at the nonrareness of conical intersections in numerical computations. So maybe it would have been worthwhile to publish a principle of the nonrareness of conical intersections to guide computational work before the nonrareness became clear by the experience of conical intersections showing up in more and more computations. It is in this spirit that we have submitted the present more detailed theorem for publication.

IV. SUMMARY

We have proved a theorem which, in plain language, says that when one encounters a local minimum (along a path) of the gap between two potential energy surfaces, almost always it is the shoulder of a conical intersection. Conical intersections are not rare; true avoided intersections are much less likely.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant No. CHE00-92019.

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