

ON A CONSISTENT QUANTUM ADIABATIC THEORY OF MOLECULES

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(Received 7 July 2009; accepted 1 September 2009)

Abstract

We point out certain inconsistency in the foundations of the standard adiabatic method in quantum theory of molecules. As an alternative, we develop a particular approach that overcomes the appointed inconsistency. Based on this new approach, some interesting physical results come to the scope. First, we point out that the adiabatic method is substantially state-of-the-molecule dependent. E.g., the method distinguishes the definite conformations as a kind of the preferred states of a molecule. Second, the existence of the local minima for the effective potential for the nuclei system appears as a kind of a necessary condition for the validity of the adiabatic method. However, our approach does not fully answer

the fundamental problem of the origin and stability of the definite (semi-classically well-defined) conformations of the large molecules. To this end, a new approach/theory is needed—as recently proposed within the context of the decoherence theory.

1 Introduction

Quantum mechanics of molecules (or quantum chemistry) relies on the adiabatic approximation. However, the "adiabatic approximation" is not unique a method. Actually, the two not-quite-equivalent methods are in parallel use. First, the method based on the adiabatic theorem [1] is based on the parameter $\kappa = m_A E_B / m_B E_A$, where m denotes the masses and E the energies of the systems A and B . If κ is much less/greater than unity, then the adiabatic approximation may work well. On the other side, the Born-Oppenheimer approximation [1-3] employs solely the mass-ratio m_A/m_B as a criterion for the validity of the approximation. In order to reconcile the two approaches, the Born-Oppenheimer method should be completed by the proper boundary conditions. E.g., for an atom, the mass ratio m_e/m_p , where e stands for the electron and p for the proton, is of the order of the adiabatic parameter for the hydrogen molecule. Yet, the protons in the atomic (non-point-like) nucleus are much faster than the atomic electrons, and the adiabatic approximation fails. The point is to introduce the boundary conditions for the protons, and thus realize that the *proper adiabatic criterion (parameter)* is the one stemming from the adiabatic theorem.

On the other side, the application of the adiabatic approximation is not fully consistent regarding the different molecular degrees of freedom. Actually, while the adiabatic parameters are typically defined relative to the original electrons- and the atomic-nuclei- degrees of freedom (the respective position-observables \hat{r}_{ei} and $\hat{r}_{N\alpha}$), the canonical transformations of the molecular degrees of freedom are employed without an independent analysis of the validity of the adiabatic approximation for the new degrees of freedom.

The existence of the definite molecular conformations (geometrical shapes) is generally used as a kind of a sufficient condition for the adiabatic approximation (cf. below) and is usually taken for granted. On the other side, existence of the local minima (that are usually interpreted as the stable conformations, in agreement with the general phenomenology of the large molecules, e.g. of biomolecules) is also taken for granted, without a theoretical derivation from the first principles (to this end cf. Refs. [4, 5]).

In this paper, we propose a slight change (at variance with the approach of Ref. [4]) in the standard procedure in quantum chemistry

and, in effect, we obtain both (i) the existence of the conformations as the preferred states within the adiabatic-approximation-method as well as (ii) we derive the existence of the local minima without resorting to phenomenology whatsoever.

2 The standard procedure: an inconsistency

In quantum chemistry, a molecule is defined as a collection of the electrons and the set of the atomic nuclei ($\mathcal{E} + \mathcal{N}$). Usually, then the adiabatic parameter $\kappa = m_e/m_\nu - e$ standing for an electron and ν for a (typical) nucleus—invokes the validity of the adiabatic approximation (valid also due to the adiabatic-theorem criterion—cf. above).

Formally, a molecule is *originally* defined by the following Hamiltonian:

$$\begin{aligned} \hat{H} &= \sum_i \hat{T}_{ei} + \sum_\alpha \hat{T}_{N\alpha} + \hat{V}_{Coul}^{(ee)} + \hat{V}_{Coul}^{(NN)} + \hat{V}_{Coul}^{(eN)} \quad \text{where} \\ \hat{V}_{Coul}^{(ee)} &= k \sum_{i,j} |\hat{r}_{ei} - \hat{r}_{ej}|^{-1}, \quad k = e^2/4\pi\epsilon_0 \\ \hat{V}_{Coul}^{(NN)} &= k \sum_{\alpha,\beta} Z_\alpha Z_\beta |\hat{r}_{N\alpha} - \hat{r}_{N\beta}|^{-1} \\ \hat{V}_{Coul}^{(eN)} &= -k \sum_{i,\alpha} Z_\alpha |\hat{r}_{ei} - \hat{r}_{N\alpha}|^{-1}. \end{aligned} \quad (1)$$

In eq. (1), \hat{T} stands for the kinetic terms (the index e standing for electrons, and N for the nuclei) while \hat{V} standing for the Coulomb interactions, where appear the original position-observables, \hat{r}_{ei} , $\hat{r}_{N\alpha}$ of the i th electron and of the α th atomic nucleus, respectively.

The semiclassical estimates justify the following general procedure: (a) from the electrons point of view, the nuclei-system is rather slow, and virtually immovable for some period of time, thus allowing one (in the zeroth order) to "freeze" the nuclei dynamics, and (b) from the nuclei-system point of view, the electrons are too fast and the nuclei dynamics may be defined by an effective Hamiltonian stemming from the averaging of the molecule's Hamiltonian over the

electrons state. Existence of the definite electrons state stems from the exact state for the $\mathcal{E} + \mathcal{N}$ system [1-3]:

$$|\Psi\rangle_{e+N} = |\phi_n(Q)\rangle_e |\chi\rangle_N + |O(\kappa^{3/4})\rangle_{e+N}. \quad (2)$$

Needless to say, the fixed values of the nuclei positions give rise to the transcription: $\hat{r}_{N\alpha} \rightarrow \vec{r}_{N\alpha} \hat{I}$ (where \hat{I} stands for the identity operator). I.e., instead of the observables, we obtain their fixed eigenvalues (appearing now as the parameters for the electrons system) for every index α . Certainly, the fixed values $\vec{r}_{N\alpha}$ give directly rise to a definite position of the center-of-mass of the nuclei system, as well as to the definite geometrical shape (conformation, \mathcal{Q}) of a molecule. So, in a sense, the existence of the definite (unique) conformation of a molecule represents a kind of a *sufficient condition* for the adiabatic approximation, which is formally defined by eq. (2) and by the following expressions.

Actually, for the fixed spatial positions of the nuclei, one may neglect the nuclei-dynamics, thus redefining the Hamiltonian eq. (1) to obtain the electrons-system Hamiltonian:

$$\hat{H}_e = \hat{T}_e + \hat{V}^{ee} + \hat{V}_e^N + const \hat{I}, \quad (3)$$

where appear the electrons-system observable following from the above transcription $\hat{V}_e^N = -k \sum_{i,\alpha} Z_\alpha |\hat{r}_{ei} - \vec{r}_{n\alpha} \hat{I}|^{-1}$, and the constant term $const \equiv k \sum_{\alpha,\beta} Z_\alpha Z_\beta |\vec{r}_{N\alpha} - \vec{r}_{N\beta}|^{-1}$; \hat{I} is the identity operator. Then one obtains the Schrodinger equation for the (time independent) Hamiltonian eq. (3), where the eigenstates can be denoted as $|\phi_n(Q)\rangle_e$ and the corresponding eigenvalues as $E_n^e(Q)$, for the different, fixed values of the nuclei positions collectively denoted as Q .

Solving the Schrodinger equation for \hat{H}_e gives rise to the Q -parameterized electrons-energy eigenvalues $E_n^e(Q)$, and for the frozen nuclei the exact state eq. (2) reads:

$$|\Psi\rangle_{e+N} = |\phi_n(Q)\rangle_e \otimes_\alpha |\vec{r}_\alpha\rangle_N, \quad \hat{r}_{N\alpha} |\vec{r}_\alpha\rangle_N = \vec{r}_{N\alpha} |\vec{r}_\alpha\rangle_N. \quad (4)$$

Now, averaging over the electrons state (that is a solution of the Schrodinger equation for the Hamiltonian eq. (3)), gives rise to the effective Hamiltonian for the nuclei system as defined by:

$$\hat{H}_N^{eff} = {}_e \langle \hat{H} \rangle_e = E_n^e(Q) + \hat{T}_N + W\hat{I}, \quad W \ll 1. \quad (5)$$

The *inconsistency* implicit in eq. (5) is as follows. In order to obtain E_n^e in eq. (5), one should: (i) apply the transcription (cf. above) $\hat{r}_{N\alpha} \rightarrow \vec{r}_{N\alpha}\hat{I}$, i.e. to "freeze" the nuclei system, and still (ii) not to neglect the nuclei kinetic energy, \hat{T}_N —in contradistinction with the derivation of eq. (3). While (i) and (ii) are implicit to derivation of eq. (5), it is really strange to investigate the dynamics of a system by freezing the system's position (the above point (i)), and still to employ the kinetic term for the "frozen" system (the above point (ii)).

This inconsistency is the true objective of the present paper. Bearing in mind that the adiabatic approximation *works well* for the plenty of the physical models and physical situations, we wonder if its physical contents (formally presented by the expressions eqs. (2)–(5)) can be obtained while avoiding the above-distinguished inconsistency. Finally, we emphasize another weak point of the standard adiabatic approximation (recently criticized in Ref. [4]): the existence of the local minima in the effective potential $E_n^e(Q)$ for the nuclei system does *not* stem from the first principles—rather, the minima are stipulated in order to fit the theory with the general experimental data.

As we show below, there exists a simple procedure that avoids the inconsistency, while giving rise to both, re-deriving the adiabatic approximation eqs. (2)–(5), as well as providing us with the interested theoretical rewards, such as the quantum-mechanical "derivation" of the local minima for $E_n^e(Q)$.

Physically, the result of the adiabatic approximation is truly remarkable. First, by reducing the exact Hamiltonian eq. (1) to the sum $\hat{H}_e + \hat{T}_N$ (as implicit to eq. (5)), it makes the system $\mathcal{E} + \mathcal{N}$ as a pair of noninteracting systems; the exact interaction \hat{V}^{eN} in eq. (1) reduces to the external field for the electrons system (cf. \hat{V}_e^N in eq. (3)), and thus produces the effective external potential for the nuclei system $E_n^e(Q)$ in eq. (5). Second, the interaction \hat{V}^{eN} that in general produces quantum entanglement (i.e. nonseparability of the subsystems and nonlocality) is managed to be written effectively as a sum of the two external potentials for the subsystems, which therefore appear effectively as approximately noninteracting systems. Needless

to say, then the total energy of a molecule is (approximately) a sum of the energies of the two systems.

However, as it directly follows from our approach, this is a *state-dependent* result—a similar argument has recently been raised in Ref. [4]. So, the domain of applicability of the adiabatic approximation is limited: in general, the subsystems \mathcal{E} and \mathcal{N} are mutually entangled, and the expression eq. (2) refers to the *very special states* of the molecule.

3 Removing the inconsistency

Our task reads: starting from the model eq. (1), to develop a procedure that, while avoiding the above-distinguished inconsistency, can still lead to the expressions of the standard adiabatic theory, eqs. (2)-(5).

Therefore, we start from the standard wisdom of the adiabatic theorem that is expressed by the points (a) and (b) of Section 2, and formally presented by the Hamiltonian eq. (3) and its corresponding Schrodinger equation:

$$\hat{H}_e|\phi_n(Q)\rangle = E_n^e(Q)|\phi_n(Q)\rangle_e, \quad (6)$$

and the corresponding state eq. (4) for the composite system $\mathcal{E} + \mathcal{N}$.

So, our starting point is the derivation of eq. (5).

To this end, we propose the *following procedure*: we add and subtract the terms \hat{V}_e^N and $const\hat{I}$ (that appear in eqs. (3) and (5)) to the total Hamiltonian \hat{H} eq. (1). The expression obtained to be substituted in ${}_e\langle\hat{H}\rangle_e$ eq. (5). Then the rhs of eq. (5) reads:

$${}_e\langle\hat{H}\rangle_e = {}_e\langle\hat{H} + \hat{V}_e^N + const\hat{I} - \hat{V}_e^N - const\hat{I}\rangle_e. \quad (7)$$

Formally, our procedure bears some similarity with the related proposal in Ref. [4]. After a closer inspection, it is clear that the two procedures do not have much in common, mathematically and/or physically.

Bearing in mind eq. (3), the rhs of eq. (7) obtains the following form:

$$\hat{H}_N^{eff} = E_n^e(Q) + \hat{T}_N + W\hat{I} + {}_e\langle\hat{V}^{eN} - \hat{V}_e^N + \hat{V}^{NN} - const\hat{I}\rangle_e. \quad (8)$$

The effective nuclei-system Hamiltonian eq. (8) differs from the original one eq. (5) by the presence of the last term on the rhs of eq. (8). Therefore, in order to deduce the standard expression eq. (5), the last term in eq. (8) should equal (at least approximately) to zero. More precisely: the desired equality to zero can not follow in the operator form—there appear the difference of the operators and of the constant terms (the c-numbers)—and therefore one should express this condition as the two simultaneously fulfilled equalities for a given state $|\chi\rangle_N$ for the nuclei system:

$${}_e\langle\hat{V}^{eN} - \hat{V}_e^N\rangle_e|\chi\rangle_N = 0, \quad (9)$$

and

$${}_e\langle\hat{V}^{NN} - \text{const}\hat{I}\rangle_e|\chi\rangle_N = 0. \quad (10)$$

Apparently, only the special set of states $|\chi_i\rangle_N$ can fulfill the equalities eqs. (9) and (10)—the adiabatic method is state dependent. As the obvious candidate in this regard appears the state eq. (4), i.e. the state of the "frozen" nuclei system:

$$|\chi\rangle_N = \otimes_{\alpha} |\vec{r}_{N\alpha}\rangle_N. \quad (11)$$

Certainly, the state eq. (11) is not an eigenstate of either of the effective Hamiltonians eq. (5) and/or eq. (8).

So, we obtain the expression eq. (11)—i.e. the existence of the definite molecules conformation(s) as implicit in the state eq. (11) and in the collective variable Q —as a kind of a necessary condition for the validity of eq. (5)—eq. (8) implies eqs. (9) and (10), which, in turn, imply eq. (11). Therefore, one may say, that the rhs of eq. (11) appears in the standard approach (cf. also eq. (4)) as a kind of a *sufficient* condition, while within our approach it appears as a kind of a *necessary* condition for the validity of eq. (5).

In the next section we emphasize that the choice of the state eq. (11) is unique as long as one deals with the exact equality in eqs. (9) and (10). For the approximate equalities in eqs. (9) and (10), one can obtain the physically convenient normalizable states instead of the state eq. (11), and to investigate the condition of the validity of eqs. (9) and (10) for virtually arbitrary instant of time t . Bearing this in mind, it becomes clear that the *kinematic* conditions eqs. (9)

and (10) do not introduce the frozen nuclei eq. (11)—the situation we wanted to avoid by the very conditions eqs. (9) and (10). The full meaning of this condition comes only from the dynamical analysis performed in the next section.

3.1 The dynamical conditions

The conditions eqs. (9) and (10) refer to a fixed instant of time. So, in order to be able within our approach to deal with eq. (5) for "every" instant of time, the states $|\chi(t)\rangle_N$ should keep the equalities eqs. (9) and (10) valid virtually for every instant of time t .

At the first sight, this seems to be a mission impossible. Actually, one should provide the states $|\chi(t)\rangle_N$ that are dynamically produced by the evolution generated by *both* \hat{H}_N^{eff} and $\hat{H}_N'^{eff}$, and to fulfill *both* the (at least approximate) equalities in eqs. (9) and (10). Interestingly and surprisingly enough, there exists such a model that *naturally* appears within our approach. To this end, we directly employ *some general quantum mechanical results without resorting to any phenomenological criteria and/or to any additional (re)interpretation of the obtained results.*

The state on the rhs of eq. (11) represents the quantum-mechanical counterpart of the exact positions of the nuclei in the classical configuration space of the nuclei system. As it is well known, these *un-normalizable* states produce the problems in a quantum-mechanical description of the "bound" physical systems, for which the normalizable states are needed. To this end, the correspondence of the unnormalizable and the normalizable states has been developed by von Neumann [6] in his theory of "macroscopic" measurements (cf. Appendix A). In effect, the unnormalizable state $|\vec{r}\rangle$ is exchanged by a gaussian (the minimal-uncertainty, i.e. the wave-packet, i.e. the "coherent") state $|\psi_{qp}\rangle$, where q is the mean value of the position- and p is the mean value of the momentum- operator for the system. A similar method has been extensively used by Omnes [7] within the microlocal analysis in the semiclassical approach to the quantum-mechanical description of the many-particle systems.

As it is distinguished in Appendix A, one may apply the following exchange of states:

$$\otimes |\vec{r}_\alpha\rangle_N \rightarrow |\Psi_{qp}\rangle_N \quad (12)$$

where appear the mean values q and p of the collective position observable \hat{Q} and of its conjugate (collective momentum) observable \hat{P} for the nuclei system, respectively. More precisely, instead of eq. (11), one may write

$$|\chi\rangle_N = |\Psi_{qp}\rangle_N, \quad (13)$$

while bearing in mind the only *approximate* (yet satisfactory—cf. Appendix A) equalities in eqs. (9) and (10).

Needless to say, up to the uncertainty relations for the collective observables \hat{Q} and \hat{P} , a normalizable state $|\Psi_{qp}\rangle_N$ bears the definite (semiclassically well-defined) molecular conformation as defined by the mean value q of the collective observable \hat{Q} . This way we fulfill the approximate equality of the effective Hamiltonians for the nuclei system for the given instant of time, $t = 0$. Let us denote the state for this instant of time as $|\Psi_{q_0 p_0}\rangle_N$. So, there remains the task of maintaining the validity of the approximate validity of eqs. (9) and (10) for the time instants $t > 0$.

Interestingly, and somewhat surprisingly enough, there exist the conditions that can fulfill the requirement of the virtual non-change of a gaussian $|\Psi_{qp}\rangle_N$ in the course of the *both* dynamics generated by the effective Hamiltonians eqs. (5) and (8).

Actually, as Hagedorn [8] (cf. also Omnes [7], p. 266, for the simpler mathematical formulation) shows: the *Schrodinger equation preserves the initial gaussian state* if the external potential is a *harmonic potential* (cf. Ref. [9] for the similar result regarding the central—e.g. the Coulomb, or the Kepler—field). More precisely: governed by the Schrodinger equation *for the harmonic potential*, the initial gaussian state $|\Psi_{q_0 p_0}\rangle_N$ evolves in time as:

$$|\Psi_{q_0 p_0}\rangle_N \rightarrow |\Psi_{q(t)p(t)}\rangle_N, \quad (14)$$

so that the *classical dynamics* $(q_0, p_0) \rightarrow (q(t), p(t))$ is governed itself by the harmonic potential—cf. Appendix B.

In the context of our considerations: the validity of eq. (14) effectively *implies* that the potential $E_n^e(Q)$ should be a polynomial of *the second order* in Q . Bearing in mind that the gaussians provide the eqs. (9) and (10) approximately to be valid, we may emphasize: if the

nuclei-system initial state is a gaussian, then the two effective Hamiltonians \hat{H}_N^{eff} and $\hat{H}_N'^{eff}$ mutually *coincide*, and the nuclei-system state is a gaussian in every instant of time—the gaussian states give rise to eq. (5) *as desired*.

The mean value q refers to the equilibrium positions of the nuclei system. So, one may conclude that the nuclei system evolves in time as the continuous change of the conformation of the molecule, where the change of the conformation (i.e. of the mean value q) follows the classical harmonic oscillations. This gives an appealing physical picture to be discussed below.

Finally, as another benefit appears a truly interesting result. The second-order polynomials bear the extremal point, i.e. the minimal value we are only interested in. Formally, such a polynomial represents a "potential well" with the well-defined *bottom* of the well. Within the standard approach, existence of the local minima in the potential $E_n^e(Q)$ is a phenomenological rule. However, within our approach, the existence of a minimum stems from the first principles: the validity of eq. (5) implies the approximate validity of eqs. (9) and (10), whose dynamical validity (referring to the nuclei-system) effectively—the validity of eq. (14) is known *only* for the harmonic potential, as well as (non-interesting for us) for the central-field potential—*requires* the harmonic potential for $E_n^e(Q)$, which unavoidably bears the well-defined bottom (the minimum value).

3.2 The origin and the stability of the molecular conformations: a problem

Within our approach, the adiabatic approximation prefers the definite conformational states of the molecule's nuclei system, in contradistinction e.g. with the atomic physics, in which the definite energy-states are preferred. E.g., the initial wave packet centered in the vicinity of the bottom of a potential well satisfies both, the equality of \hat{H}_N^{eff} eq. (5) and $\hat{H}_N'^{eff}$ eq. (8), as well as bears stability of its form in the course of time, eq. (14). This time interval equals infinity for the *exactly harmonic* potential for the molecular conformations \hat{Q} [7, 8].

In the vicinity of the bottom of the potential well, the mean value $q = \langle \hat{Q} \rangle$ (that defines the molecule conformation) changes in accordance with the *classical law* for the harmonic oscillator. Physically, it

means that, in the vicinity of the local minimum (for which, as we see, the adiabatic method is expected to work properly), one *does not deal with the unique conformation*. Rather, there appears the continuous, classical-physics-described harmonic change of the molecule conformation. Certainly, for the small amplitudes, the different conformations can not be macroscopically distinguished, while they bear the slightly different mean-energies, ${}_N\langle\Psi_{q(t)p(t)}|\hat{H}_N^{eff}|\Psi_{q(t)p(t)}\rangle_N = f(t)$.

In general (cf. below), the coherent superpositions of the wave packets need not satisfy the conditions eq. (9) and (10). So, we conclude that the adiabatic approximation need not be valid for the states out of the local minimum and/or for the arbitrary superpositions of the gaussian (wave packet) states.

For the *realistic* systems, one can hardly expect the exact harmonic character of the potential—typically, there appear the non-negligible anharmonic terms in the potential. In this case, needless to say, the gaussian states do not satisfy "robustness" as defined by eq. (14). In effect, the dynamics of the initial gaussian is transformed into a coherent superposition of the different gaussian states. On the other side, our considerations do not forbid the existence of more-than-one local minimum for the conformation-system potential. While our analysis establishes validity of the general results, eqs. (2)-(5), for every *single* local minimum (the bottom of a potential well), it does not fully describe the dynamics of the arbitrary superpositions of the gaussian states—cf. the next section.

The following question is fundamental in quantum mechanics of molecules [10]: why certain molecules (e.g. macromolecules) usually bear the definite conformation, instead of having the definite energy? To this end, our approach offers the following *yet incomplete answer*: if the initial state is a gaussian (centered around the very bottom of the potential well), then in the exact harmonic potential it will remain a gaussian "forever"—to this end, the gaussian states bear robustness (the dynamical stability) as expected for the large-molecules conformations. However, as we show below, even certain coherent superpositions of the gaussian states can satisfy eq. (5) as well formally as the "robustness", thus not allowing one to ascribe a definite conformation to a molecule in such states. In general, however, the arbitrary coherent superpositions of the gaussian states—as it can be expected—do not satisfy eq. (5), thus giving rise to both, the

limitation of the adiabatic method within our approach, as well as leaving the above-distinguished problem open. To this end, it seems that a new theory is needed—it seems that the so-called decoherence theory might clear the terrain in a consistent way [11].

4 Discussion

We try to avoid the inconsistency implicit in the derivation of eq. (5). To this end, we employ certain general quantum-mechanical results—cf. Appendices A and B. This gives rise (cf. eqs. (9) and (10)) to the quantum-state-dependent applicability of the general formulas eq. (2)-(5) of the standard adiabatic method in quantum mechanics of molecules. In effect, the existence of a minimum of the effective potential for the nuclei system appears as a kind of the necessary condition for the method—apart from the non-interesting central field, the harmonic potential appears as the only candidate for the validity of eq. (14). Interestingly enough—and in contradistinction with the standard approach—this result follows from the *first principles*, without resorting to phenomenology.

Our approach does not *per se* forbid the coherent superpositions of the different conformations states, neither it establishes the unique local minimum for the potential. Interestingly enough, certain superpositions of conformations can still match the adiabatic method—i.e. to satisfy both, eqs. (9) and (10), as well as eq. (14)—cf. Appendix C. [Some of these superpositions might be recognized as the energy eigenstates for the vibrational degrees of freedom of the molecule's nuclei-system (for comparison cf. the model of the small-molecules chirality [12, 13]).]

However, the arbitrary superpositions of the conformational states do not justify eq. (5), and this is the instance at which our considerations departure from the standard adiabatic method—then the effective Hamiltonians eq. (5) and eq. (8) are not mutually equal. So, in such cases, one is obliged to deal with the exact Hamiltonian eq. (1), which, while bearing the interaction term \hat{V}^{eN} , gives in general rise to the quantum *entanglement* in the composite system $\mathcal{E} + \mathcal{N}$ [12]. Having this in mind, it becomes evident how restrictive, and how-much-convenient *is* the state eq. (2).

Therefore, the following (mutually related) questions remain open within the standard, likewise within our approach: why, after all, the

initial state of the nuclei system would be a gaussian? (the universally valid quantum mechanics does not set any limitations in this regard—cf. also the Ref. [10]); how can we treat the arbitrary superpositions of the gaussian states as the possible cases not properly described by the adiabatic approximation?; why the small molecules are usually described by energy (not yet bearing the definite conformation), and the large molecules are typically described by their spatial conformations (without the definite energy)—the former being qualitatively modeled by the state eq. (21) of Appendix C, while the later being described by eq. (13)? To this end, we believe, a new physical theory is needed as recently proposed and elaborated in Ref. [11]—that is our conclusion.

An independent analysis concerning the alternative description of a molecule by introducing the nuclei-system center-of-mass and the "relative coordinates" (that directly introduce the molecule conformation) will be separately presented.

Appendix A

For simplicity, let us consider a one-dimensional system defined by the continuous position-observable \hat{x} and its conjugate (also continuous) momentum \hat{p} ; $[\hat{x}, \hat{p}] = i\hbar$.

"Coarse graining" of the real axis into the segments of the width δx can give the approximations of the exact position-observable eigenstates $|x\rangle$. Actually, every segment of the real axis $[q - \delta x/2, q + \delta x/2]$, centered around the value q , can be properly approximated by a gaussian state $|\Psi_{qp}\rangle$, if $\langle \hat{x} \rangle = q$ and $\langle \hat{p} \rangle = p$, while the standard deviation of \hat{x} in this state, $\Delta \hat{x}$, is of the order of δx . This way, the exact eigenvalues x of \hat{x} and the corresponding eigenstates $|x\rangle$ are properly approximated by q and $|\Psi_{qp}\rangle$, respectively. An extensive analysis in this regard can be found in Omnes [7].

The form of the gaussian states does not depend on the system's dimensionality. The set of these states is overcomplete and there are not the exactly-orthogonal pairs of these states. Nevertheless, even if orthonormalized (then defining a nonunique orthonormalized basis $|\Psi_{\mu\nu}\rangle$), these states maintain the approximate quantum-mechanical description of the exact position-observable eigenstates.

Actually, von Neumann [6] shows that the observables \hat{x} and \hat{p} can be properly approximated by the discrete observables $\hat{\xi}$ and $\hat{\pi}$, $[\hat{\xi}, \hat{\pi}] = 0$, and their common eigenstates $|\Psi_{\mu\nu}\rangle$ constitute an orthonormalized basis. Interestingly enough, the minimal uncertainty condition $\epsilon\eta = \hbar/2$ is only linearly increased. Namely, one can write:

$$\|(\hat{x} - \hat{\xi})|\Psi_{\mu\nu}\rangle\| \leq C\epsilon, \quad \text{and} \quad (15)$$

$$\|(\hat{p} - \hat{\pi})|\Psi_{\mu\nu}\rangle\| \leq C\eta, \quad (16)$$

while $C < 60$ [6].

So, even the more general states $|\Psi_{\mu\nu}\rangle$ can be used in order (nonuniquely) to approximate the position-observable eigenstates. For the reasons made explicit in the body text, we shall further refer to the non-orthogonal gaussian states $|\Psi_{qp}\rangle$ for the purpose of approximating the position-observable exact eigenstates $|\vec{r}\rangle$, as assuming:

$$\|_e\langle \hat{V}^{eN} - \hat{V}_e^N \rangle_e |\Psi_{qp}\rangle_N\| \ll 1, \quad \|_e\langle \hat{V}^{NN} - \text{const.}\hat{I} \rangle_e |\Psi_{qp}\rangle_N\| \ll 1. \quad (17)$$

Appendix B

For a system of the arbitrary number of the degrees of freedom, denoted collectively as \hat{Q} , Hagedorn [8] (see also Omnes [7], p. 266) was able to show that the *Schrodinger dynamics preserves the gaussian states* as:

$$\exp(-it\hat{H}/\hbar)|\Psi_{q_0 p_0}\rangle = |\Psi_{q(t)p(t)}\rangle, \quad (18)$$

if for the Hamiltonian $\hat{H} = \hat{T} + U(\hat{Q})$ —the potential $U(\hat{Q})$ is *at most the second-order polynomial* in \hat{Q} , while the *classical* dynamics $(q_0, p_0) \rightarrow (q(t), p(t))$ is governed by the classical counterpart of the harmonic potential \hat{U} ; $q = \langle \hat{Q} \rangle$ and $p = \langle \hat{P} \rangle$, while $[\hat{Q}, \hat{P}] = i\hbar$. Physically, the mean values of both \hat{Q} and \hat{P} follow the *harmonic-oscillator trajectories in the classical phase space*, while the quantum oscillations (the observable \hat{Q}) refer to instantaneous conformation (i.e. the equilibrium position) q in an instant of time t .

The second order-polynomial $U(Q)$ defines a "potential" well with the well defined *minimum*—i.e. the bottom of the well. Now, according to the Legend-Dirichle theorem, the very bottom of the potential represents a stable point (the equilibrium point) for the harmonic oscillations around the bottom. Physically, the bottom of the potential well formed by the parabolic potential $U(Q)$ represents the one (not necessarily the unique) stable conformation of the molecule. Needless to say, this way we conclude that existence of the local minima in the effective potential $U(Q)$ for the molecule nuclei-system stems from the first principles, without calling for any phenomenology whatsoever.

Appendix C

Let us rewrite eqs. (9) and (10) as:

$${}_e\langle\hat{V}^{eN} - \hat{V}_e^N\rangle_e|\Psi_{qp}\rangle_N = |\epsilon\rangle_N, \quad \epsilon \equiv |||\epsilon\rangle_N|| \ll 1 \quad (19)$$

and

$${}_e\langle\hat{V}^{NN} - \text{const}\hat{I}\rangle_e|\Psi_{qp}\rangle_N = |\epsilon'\rangle_N, \quad \epsilon' \equiv |||\epsilon'\rangle_N|| \ll 1. \quad (20)$$

Let us consider a superposition

$$|\chi\rangle_N = c_1|\Psi_{q_1p_1}\rangle_N + c_2|\Psi_{q_2p_2}\rangle_N, \quad (21)$$

where $|\Psi_{qp}\rangle_N$ s satisfy eqs. (19) and (20); the corresponding ϵ s can be denoted respectively as ϵ_1 and ϵ_2 . Then one can easily prove the inequality:

$$||{}_e\langle\hat{V}^{eN} - \hat{V}_e^N\rangle_e|\chi\rangle_N|| \leq 2\epsilon \ll 1, \quad (22)$$

where ϵ is the average for $\epsilon_i, i = 1, 2$. On the other side, the state $|\chi\rangle_N$ satisfies the Schrodinger law, as a consequence of the linearity of the Schrodinger law, and in accordance with eq. (14) for $|\Psi_{qp}\rangle$ s appearing in eq. (21). So, one may conclude that even certain coherent superpositions of the conformational states can satisfy eq. (5), i.e. justify applicability of the adiabatic approximation.

However, the arbitrary coherent superpositions,

$$\sum_{i=1}^L c_i |\Psi_{q_i, p_i}\rangle, \quad (23)$$

need not satisfy eq. (5) as—in analogy with eq. (22)—one obtains $L\epsilon$ that need not be a small number. Since all the analogous conclusions can follow for eq. (20), one can conclude that the arbitrary superpositions of the gaussian states need not satisfy eq. (5)—i.e., as it stems from eqs. (8)-(10), the adiabatic approximation need not be applicable for the arbitrary superpositions of the gaussian states.

References

- [1] A. Messiah, "Quantum Mechanics", North Holland Publ. Comp., Amsterdam, 1976
- [2] P. Atkins, R. Friedman, "Molecular Quantum Mechanics", Oxford Univ. Press, Oxford, UK, 2005
- [3] M. V. Volkenstein, L. A. Gribov, M. A. El'shevich, B. I. Stepanov, "Molecular Vibrations", Nauka, Moscow, 1972 (in Russian)
- [4] L. A. Gribov and Y. B. Magarshak, *Conc. Phys.* **V**, 191 (2008)
- [5] L.A. Gribov, S.P. Mushtakova, "Quantum Chemistry", Gardariki, Moscow, 1999 (in Russian)
- [6] J. von Neumann, "Mathematical Foundations of Quantum Mechanics", Princeton Univ. Press, Princeton, USA, 1955
- [7] R. Omnes, "The Interpretation of Quantum Mechanics", Princeton Univ. Press, Princeton, USA, 1996
- [8] G. Hagedorn, *Commun. Math. Phys.* **77**, 1 (1980)
- [9] M. Nauenberg, *Phys. Rev. A* **40**, 1133 (1989)
- [10] M. Quack, *Angew. Chem. Int. Ed. Engl.* **26**, 571 (1989)
- [11] J. Jeknić-Dugić, *Europ. Phys. J. D* **51**, 193 (2009)

- [12] M. Giulini et al, "Decoherence and the Appearance of a Classical World in Quantum Theory", Springer, Berlin, 1996
- [13] G. Jona-Lasinio, P. Claverie, Prog. Theor. Phys. Suppl. **86**, 54 (1986)