PHYSICAL REVIEW A VOLUME 36, NUMBER 4 AUGUST 15, 1987

Chemical physics without the Born-Oppenheimer approximation: The molecular coupled-cluster method

Hendrik J. Monkhorst*
Institute "Rudjer Bosković," 41001 Zagreb, Croatia, Yugoslavia

(Received 12 March 1987)

The Born-Oppenheimer (BO) and Born-Huang (BH) treatments of molecular eigenstates are reexamined. It is argued that in application of the BO approximation to nonrigid molecules and chemical dynamics involving single potential-energy surfaces (PES's), errors on the order of tens of percents can easily occur in many computed properties. Introduction of a BH expansion (in BO states) will always lead to poor convergence when the BO approximation fails; its diagonal (or adiabatic) approximation will not change this situation. The main problem in the above applications is the absence of well-developed, well-separated minima in the PES (or no minima at all). Inspired by a non-BO view of a molecule by Essén [Int. J. Quantum Chem. **12**, 721 (1977)], a molecular coupled-cluster (MCC) method is formulated. An Essén molecule consists of neutral subunits ("atoms"), weakly interacting ("bonds") in some spatial arrangement ("structure"). The quasiseparation in collective and individual motions within the molecule comes about by virtue of the virial theorem, not the smallness of the electron-to-nuclear mass ratio. The MCC method not only should converge well in the cluster sizes, but it also is capable of describing electronic shell and molecular geometric structures. It can be viewed as the workable formalism for Essén's physical picture of a molecule. The time-independent and time-dependent versions are described. The latter one is useful for scattering, chemical dynamics, laser chemistry, half-collisions, and any other phenomena that can be described as the time evolution of many-particle wave packets. Close relationship to time-dependent Hartree-Fock theory exists. A few implementational aspects are discussed, such as symmetry, conservation laws, approximations, numerical techniques, as well as a possible relation with a non-BO PES. Appendixes contain mathematical details.

I. INTRODUCTION

Molecular physics and quantum chemistry are dominated by the Born-Oppenheimer (BO) approximation[1] and its most important consequence, the potential-energy surface (PES) concept. A PES is usually defined as the eigenvalue $E_e(R)$ of the clamped-nucleus electronic Hamiltonian for all nuclear configurations R. Different eigenvalues lead to different surfaces in $(3N_n-6)$- $[(3N_n-5)$ for linear molecules] dimensional spaces, where N_n is the number of nuclei (or atoms) in the molecule. The PES concept has made, and continues to make, a profound impact on chemical physics. Not only does it provide a precise and computable meaning to molecular structure in a quantum context as the nuclear configuration R_0 for which the PES is a minimum, it pervades the thinking and conceptualization of virtually all subdisciplines of chemistry.

The advantages of the PES construct are undeniable. The elimination of the electronic degrees of freedom from the picture of a molecule and its properties, particularly on its lowest PES, is a great simplification. Concepts such as internal rotation barriers, transition states, isomerization, etc., can be understood, at least qualitatively. Dissociation also has a nice and computable expression with a PES. Electronic excitations as transitions between two PES's, with nuclear-dynamics-generated broadenings, shifts, and intensity changes, are other examples. The whole of infrared and microwave spectroscopy is unthinkable without a PES. Finally, chemical dynamics and various scattering phenomena involving atoms and/or molecules, regardless of their classical, semiclassical, or quantum descriptions, rely heavily on these surfaces. Thus the industry of calculating PES's in computational quantum chemistry was spawned.[2]

But we should not close our eyes to the shortcomings of the PES concept. Not surprisingly, the limitations and errors that are gradually being accumulated, particularly under the probing of high-resolution laser spectroscopies and accurate scattering experiments, are caused by the very elimination of the electronic degrees of freedom. Interaction among PES's, problems near (avoided) crossings, intersurface jumping, etc., are manifestations that this total elimination is physically unacceptable. In principle one can improve upon the BO approximations by introducing the so-called Born-Huang (BH) expansion.[3] This expansion uses the electronic eigenstates $\Psi_e(r,R)$ associated with the PES $E_e(R)$ as a basis for the molecular wave function $\Psi(r,R)$. Ψ_e must be known for all R and for all electronic quantum numbers including the continuum. This is obviously an awesome task, and it has never been implemented to convergence. Only the adiabatic (or diagonal) approximation to the BH expansion preserves the single PES. All other truncations involve interactions among them, thus eliminating many conceptual niceties of the PES concept.

Quite independent of the problems connected with the implementation of the BO approximation, a debate evolved in the literature between 1976 and 1982 concerning the relationship between quantum theory and molecular structure. This exchange was initiated with an article by Woolley[4] and quieted (albeit not settled) in 1982 by Claverie[5] (see also the references cited in Ref. 5). The main theme of the debate was the impossibility to reconcile the notion of molecular structure with quantum theory because of the classical nature of the former. The articles revealed the profound schism between the ways chemists view and treat electrons (as quantum particles) and nuclei (as classical particles), the latter being the carriers of the classical way of thinking in chemistry. At the heart of this dichotomy is the BO approximation, which must be viewed as the culprit of the apparent conflict. Although the debate ended inconclusively, it had the salutary effect of raising the prospect that there may be a problem, and that the BO approximation is not sacred, or even uniquely reliable in all cases. In my opinion the most constructive critique of the BO approximation was provided by Essén.[6] His telling conclusion is that the form of the Coulomb interaction, and not the smallness of the electron-to-nuclear mass ratio, is responsible for the approximate separation of collective and individual internal molecular motion. (This separation leads to the spectroscopic sequences associated with rotational, vibrational, and electronic excitations which inspired the BO approximation in the first place.) Although Essén did not provide a workable formalism, his arguments are compelling and the resulting framework is intriguing. Invoking only the virial theorem for Coulombic forces and treating all particles on an equal footing, a molecule according to Essén can be viewed as an aggregate of nearly neutral subsystems ("atoms") that interact weakly ("chemical bonds") in some spatial arrangement ("molecular structure"). No adiabatic hypothesis, or interpretation, as in the BO approximation, is made, and the analysis should hold for all bound states.

In this paper I would like to propose the use of the coupled-cluster (CC) method for treating the electrons and atomic nuclei of a molecule on the same quantum dynamical footing. I will argue that the time-independent CC method is ideally suited for bound states, and the time-dependent version for any scattering state describable as a time-evolving many-particle wave packet. I will also conclude that bound and scattering states alike can be described with the same cluster truncation. There will be no PES, only cluster operators that can provide structurelike correlation among nuclei. My proposal can be viewed as the beginnings of a practical implementation of Essén's molecule. Yet, by including scattering states the proposal also goes beyond his view. To stress the physical content of my approach the details of the formalism are left to later publications; only a bare minimum in notation and definitions will be presented. Experience with the CC method in very varied contexts will be used to support my proposal.

In Sec. II I have revisited the analysis by Born and Oppenheimer and of the BH expansion. I will point out the most important requirements underlying the BO approximation (which are usually forgotten), and stress their consequences (which are equally ignored). Moreover, a more complete and careful discussion is given of the effects of the elimination of the center-of-mass (c.m.) motion. These effects are largely ignored in the original BO and BH treatments. Essén's view of a molecule will be presented in some detail, with emphasis on the qualitative physical ideas. This section serves to set the stage for leaving the PES concept.

In Sec. III I present the arguments in favor of a molecular coupled-cluster (MCC) method. After a brief survey of some crucial results with the CC method for identical particles, I formulate the time-independent and time-dependent MCC approximations. Some formal and implementational questions are raised.

In Sec. IV I outline the program for future theoretical and numerical developments to bring the MCC method to life. Obviously, many questions need to be pursued, and the outline can be only preliminary. Section V contains a summary and concluding remarks. Three Appendixes are added on the reduction of an N-body to an $(N-1)$-body problem on mathematical details, and on the invariance of internal angular momentum to internal coordinate transformations.

II. PRESENT STATUS OF MOLECULAR QUANTUM THEORY

A. Preliminaries, notation, and definitions

In the BO analysis[1] and BH expansion[3] the presence of the nuclear kinetic energy operator, denoted by K_n, is considered as a perturbation. Since typical electron and nuclear momenta are comparable[6] (see also Sec. II E below), $\langle K_n \rangle$ values scale like M_n^{-1} (at least for ground and low-lying states) with M_n a nuclear mass. Therefore we have

$$\frac{\langle K_n \rangle}{\langle K_e \rangle} \sim \frac{m_e}{M_n} , \tag{1}$$

with K_e the electronic kinetic energy operator, and m_e the electron mass. The smallness of (m_e/M_n), with values of $10^{-6} \div 10^{-4}$ for typical molecules, is obviously a compelling reason to treat K_n as a perturbation. However, as we will see below, a more relevant perturbation parameter is provided by

$$\kappa = (m_e/\overline{M})^{1/4} , \tag{2}$$

where $\overline{M}$ is the largest nuclear mass, with typical values $\kappa \sim 10^{-1}$. Below I will point out that in many applications of the BO approximation such κ values are disturbingly large.

As usual in perturbative expansions, no analysis is attempted to determine the radius of convergence in κ. The fact that the kinetic energy operator is singular suggests at best asymptotic convergence.[7] This possibility makes it imperative to determine carefully the limitations of the BO approximation.

In the original BO (Ref. 1) and BH (Ref. 3) analyses no explicit separation of the c.m. motion was made. As a result the treatment of the kinetic energy operator was somewhat unsatisfactory since the scaling with κ is then unclear. In this paper I will eliminate this problem and develop the theory for a manifestly internal molecular Hamiltonian.

H_M is the total molecular Hamiltonian

$$H_M = K_M + V \ , \tag{3}$$

where K_M is the total kinetic energy operator, and V is given by

$$V = V_{ee} + V_{en} + V_{nn} \ . \tag{4}$$

V_{ee}, V_{en}, and V_{nn} are the electron-electron, electron-nuclear, and nuclear-nuclear potential-energy operators, respectively. In Appendix A I have shown [see Eqs. (A10)–(A14)] that K_M can be written as

$$K_M = K_{\text{c.m.}} + K \tag{5}$$

with $K_{\text{c.m.}}$ the molecular c.m. and K the internal kinetic energy operator. For the purposes of this section I will express K as follows:

$$K = K_e + K_n + K_{ee} + K_{en} + K_{nn} \ , \tag{6}$$

where

$$K_e = \sum_e \frac{p_e^2}{2\mu_e} \ , \tag{7}$$

$$K_n = \sum_n{}' \frac{p_n^2}{2\mu_n} \ , \tag{8}$$

$$K_{ee} = \overline{M}^{\,-1} \sum_{(e<e')} \mathbf{p}_e \cdot \mathbf{p}_{e'} \ , \tag{9}$$

$$K_{en} = \overline{M}^{\,-1} \sum_{e,n}{}' \mathbf{p}_e \cdot \mathbf{p}_n \ , \tag{10}$$

$$K_{nn} = \overline{M}^{\,-1} \sum_{(n<n')}{}' \mathbf{p}_n \cdot \mathbf{p}_{n'} \ , \tag{11}$$

$\mathbf{p}_e$ and $\mathbf{p}_n$ are the electron and nuclear momentum operators associated with the position vectors $\mathbf{r}_e$ and $\mathbf{r}_n$ relative to the heaviest nucleus with mass $\overline{M}$. The primes on the n sums in Eqs. (8), (10), and (11) indicate the omission of the heaviest nucleus. (As explained below, this nucleus will be at the center of a molecular shell structure.) The reduced masses μ_e and μ_n are given by

$$\mu_e^{-1} = m_e^{-1} + \overline{M}^{\,-1} = \left[1 + \frac{m_e}{\overline{M}} \right] m_e^{-1} \ , \tag{12}$$

$$\mu_n^{-1} = m_n^{-1} + \overline{M}^{\,-1} = \frac{m_e}{\overline{M}} \left[1 + \frac{\overline{M}}{m_n} \right] m_e^{-1} \ . \tag{13}$$

The last equalities in Eqs. (12) and (13) are added in preparation for the expansion of H in powers of κ given below. For notational convenience I denote with r and R the set of electron and nuclear coordinates $\{\mathbf{r}_e\}$ and $\{\mathbf{r}_n\}$, respectively. R_0 denotes the so-called "equilibrium" nuclear configuration $\{\mathbf{r}_{n0}\}$, which is central to the BO analysis.

B. The BO approximation

Consider the Schrödinger equation

$$(H - E)\Psi(r,R) = 0 \tag{14}$$

for the molecular problem, where H is given by

$$H = K + V \ , \tag{15}$$

with K and V defined above. We wish to relate the solutions of Eq. (14) to those of a clamped-nucleus electronic Schrödinger problem which we will define presently.

Assuming Eq. (2) for κ, which will be justified *ex post facto* below, we can express H as a power series in κ. This will be possible under the following assumptions,[1,3] the significance of which will become evident shortly.

Assumption 1. The nuclear motion described by Ψ will be confined to a small vicinity of R_0 such that $(R - R_0)$ can be considered small expressed by

$$\mathbf{r}_n - \mathbf{r}_{n0} = \kappa \mathbf{U}_n \ . \tag{16}$$

Assumption 2. $\Psi(r,U)$, with $U = \{U_{nx}, U_{ny}, U_{nz}\}$, the collection of nuclear displacement coordinates defined by Eq. (16), is essentially different from zero only in domains of r and U that are comparable in extent. The actual smallness of the nuclear displacements from R_0 is accounted for by the scale parameter κ.

With Eq. (16) we obviously have

$$\partial/\partial \mathbf{r}_n = \kappa^{-1} \partial/\partial \mathbf{U}_n \ , \tag{17}$$

leading to the useful definition

$$\mathbf{P}_n = \kappa \mathbf{p}_n \ . \tag{18}$$

We can now express Eq. (15) alternatively

$$H = H_0 + H_1 \ , \tag{19}$$

where

$$H_0 = K_e^{(0)} + V \ , \tag{20}$$

$$H_1 = \kappa^2 (K_n^{(2)} + K_{nn}^{(2)}) + \kappa^3 K_{en}^{(3)} + \kappa^4 (K_e^{(4)} + K_{ee}^{(4)}) \ , \tag{21}$$

with the definitions

$$K_e^{(0)} = \sum_e \frac{p_e^2}{2m_e} \ , \tag{22}$$

$$K_n^{(2)} = \sum_n{}' \left[1 + \frac{\overline{M}}{m_n} \right] \frac{P_n^2}{2m_e} \ , \tag{23}$$

$$K_{nn}^{(2)} = \sum_{(n<n')}{}' \frac{\mathbf{P}_n \cdot \mathbf{P}_{n'}}{m_e} \ , \tag{24}$$

$$K_{en}^{(3)} = \sum_{e,n}{}' \frac{\mathbf{p}_e \cdot \mathbf{P}_n}{m_e} \ , \tag{25}$$

$$K_e^{(4)} = K_e^{(0)} \ , \tag{26}$$

$$K_{ee}^{(4)} = \sum_{(e<e')} \frac{\mathbf{p}_e \cdot \mathbf{p}_{e'}}{m_e} \ . \tag{27}$$

We will call H_0 the *clamped-nucleus electronic Hamiltonian,* since it contains no nuclear dynamic terms. Its eigenfunctions satisfy the Schrödinger equation

$$[H_0 - E_e(R)]\Psi_e(r,R) = 0 \ , \tag{28}$$

with e denoting electronic quantum numbers, and R appears only parametrically. In order to relate Ψ to Ψ_e we make another assumption:[3]

Assumption 3. $\{E_e(R),\Psi_e(r,R)\}$ are known and well defined for a certain nuclear configuration R_0 and all neighboring configurations R. This assumption implies the breakdown of the analysis below if R_0 is at or near crossings of PES's defined by $E_e(R)$.

Under the above assumptions we can solve Eq. (28) perturbatively, invoking the expansions in R around R_0

$$H_0=H_0(r,R_0+\kappa U)=H_0^{(0)}+\kappa H_0^{(1)}+\kappa^2 H_0^{(2)}+\cdots , \tag{29}$$

$$E_e(R)=E_e^{(0)}+\kappa E_e^{(1)}+\kappa^2 E_e^{(2)}+\cdots , \tag{30}$$

$$\Psi_e(r,R)=\Psi_e^{(0)}+\kappa\Psi_e^{(1)}+\kappa^2\Psi_e^{(2)}+\cdots . \tag{31}$$

All superscripted terms are homogeneous functions of U_{ni} of degree equal to superscript value. We assume the perturbative solution of Eq. (28) to be completed to any order.

Before proceeding to solve Eq. (14), I will justify Eq. (2) for κ. According to Assumption 1, the nuclear motion is expected to be oscillatory around R_0. We can then state

$$\langle K_n+K_{nn}\rangle_\Psi\simeq\langle V(R)-V(R_0)\rangle_\Psi , \tag{32}$$

similar to the virial theorem for the harmonic oscillator. Using the relationship

$$\begin{aligned} V(R)-V(R_0)&=H_0(R)-H_0(R_0)\\ &=\kappa H_0^{(1)}+\kappa^2 H_0^{(2)}+O(\kappa^3) \end{aligned} \tag{33}$$

and assuming

$$\langle U_{ni}\rangle_\Psi=0 \tag{34}$$

for all n,i, which is consistent with the oscillatory nuclear motion, we can write

$$\langle K_n+K_{nn}\rangle_\Psi\simeq\kappa^2\langle H_0^{(2)}\rangle_\Psi+O(\kappa^3) . \tag{35}$$

On the other hand, we can write [see Eqs. (8), (11), (13), (17), (23), and (24)]

$$\langle K_n+K_{nn}\rangle_\Psi=\kappa^{-2}\frac{m_e}{\overline{M}}\langle K_n^{(2)}+K_{nn}^{(2)}\rangle_\Psi . \tag{36}$$

Therefore, we arrive at the relationship

$$\kappa^{-2}\frac{m_e}{\overline{M}}\langle K_n^{(2)}+K_{nn}^{(2)}\rangle_\Psi\simeq\kappa^2\langle H_0^{(2)}\rangle_\Psi . \tag{32$'$}$$

At this point it is timely to remember Assumption 2, and to introduce the following observation: when defining a perturbative expansion parameter for the Hamiltonian as well as its eigenfunctions, the coefficients of κ^n should be of comparable magnitude, i.e., the expectation values appearing in Eqs. (32′) should be comparable. In view of Assumptions 1 and 2 the reader can easily see that the operators of Eqs. (19)–(27) and (29) satisfy this requirement. But then it follows from Eq. (32′) that κ should satisfy an equation like

$$\kappa^{-2}\frac{m_e}{\overline{M}}=\kappa^2 , \tag{37}$$

which leads to Eq. (2). Notice that this result is not unique; $\overline{M}$ can be replaced by a nuclear mass different from the heaviest one. However, the crucial point of Eq. (37) is the behavior of κ like the *one-fourth power* to $(m_e/\overline{M})$. This behavior determines its magnitude. A different derivation of Eq. (2), starting from the BH expansion, has been given by Kresin and Lester.[8] Their derivation relies on the supposition that nuclear and electronic motions are approximately harmonic with comparable force constants. This supposition is similar to Eq. (32) and the requirement of comparable expectation values to perturbation operators.

We can now proceed to solve the exact Schrödinger equation (14) by the usual perturbation method,

$$E=E^{(0)}+\kappa E^{(1)}+\kappa^2 E^{(2)}+\cdots , \tag{38}$$

$$\Psi=\Psi^{(0)}+\kappa\Psi^{(1)}+\kappa^2\Psi^{(2)}+\cdots . \tag{39}$$

The details are subtle, and somewhat involved albeit straightforward, for which I refer the reader to Appendix B and the original articles.[1,3] For this paper the two most significant results are (1) in order to continue the solution of the equations beyond zeroth order at all, R_0 must be the equilibrium configuration, i.e.,

$$E_e^{(1)}=[\partial E_e(R)/\partial R]_{R=R_0}=0 , \tag{40}$$

Eq. (40) arises from one of the solubility conditions. (See Appendix B.) (2) The so-called adiabatic separability of nuclear and electronic coordinates is only possible through second order in κ, i.e.,

$$\Psi(r,U)=[X^{(0)}(U)+\kappa X^{(1)}(U)+\kappa^2 X^{(2)}(U)]\Psi_e(r,U) , \tag{41}$$

with $X^{(i)}$ determined by linear inhomogeneous equations. When Eq. (40) is not satisfied, separability is impossible beyond zeroth order. Equation (41) is usually called the *Born-Oppenheimer approximation* (or BO *separation*) to the molecular wave function Ψ.

In my judgement these two results, and Assumptions 1–3, are insufficiently appreciated in many applications of the BO separation. Before discussing their consequences I will review the BH expansion as the supposed alternative to the BO analysis.

It is interesting to note that the terms $K_{en}^{(3)}$ and $(K_e^{(4)}+K_{ee}^{(4)})$ do not affect the above results, since they contribute to H only in third and fourth order in κ and, consequently, to E. However, in discussions of the rotational fine structure of the molecular spectrum these terms must be included.[3]

C. The Born-Huang expansion

We can adopt the point of view that the solutions $\{E_e,\Psi_e\}$ provide a complete set of states with which to expand the exact state $\Psi(r,R)$.[3] Although one has to include the continuum states, it is anticipated that for the low-lying bound states Ψ, it is sufficient to restrict consideration to bound Ψ_e states only. Thus we write

$$\Psi(r,R)=\textstyle\sum_e X_e(R)\Psi_e(r,R) . \tag{42}$$

Substituting this expansion in Eq. (14), multiplying with

$\Psi_e^*(r,R)$, and integrating over r, we obtain

$$\sum_{e'} \langle \Psi_e \mid H_0+H_1-E \mid \Psi_{e'} \rangle_r X_{e'}(R)=0 \ . \tag{43}$$

Substituting expressions (20) and (21) for H_0 and H_1, respectively, several terms occur. Using Eqs. (7)–(11) and (22)–(28) we can summarize the result as

$$[K_n+K_{nn}+E_e(R)-E]X_e(R)=\sum_{e'} C_{ee'}X_{e'}(R) \ . \tag{44}$$

$C_{ee'}$ are operators given by

$$C_{ee'}=\langle \Psi_e \mid H_1 \mid \Psi_{e'} \rangle_r + \sum_n{}' \mu_n^{-1} \langle \Psi_e \mid \mathbf{p}_n \mid \Psi_{e'} \rangle_r \cdot \mathbf{p}_n$$
$$+\overline{M}^{\,-1} \sum_n{}' \left\langle \Psi_e \left| \sum_{e''} \mathbf{p}_{e''} + \sum_{(n' \neq n)}{}' \mathbf{p}_{n'} \right| \Psi_{e'} \right\rangle_r \cdot \mathbf{p}_n \ , \tag{45}$$

where it is to be understood that the factors $\langle \ \rangle_r$ are c numbers (H_1 and $\mathbf{p}_n$ operate only on $\Psi_{e'}$). Since the bound states Ψ_e can be chosen real, it can be shown that

$$C_{ee}=C_{ee}(R)=\langle \Psi_e \mid H_1 \mid \Psi_e \rangle_r \tag{46}$$

(i.e., the last two terms vanish identically), and C_{ee} is a multiplicative operator. Therefore we can write instead of Eq. (44)

$$[K_n+K_{nn}+U_e(R)-E]X_e(R)=\sum_{(e' \neq e)} C_{ee'}X_{e'}(R) \ , \tag{47}$$

where I have introduced

$$U_e(R)=E_e(R)-C_{ee}(R) \ . \tag{48}$$

According to Eq. (21), H_1 contains terms that scale like κ^2 to κ^4. If we only keep terms of order κ^2, we get

$$C_{ee}(R) \simeq \langle \Psi_e \mid K_n+K_{nn} \mid \Psi_e \rangle_r \ . \tag{49}$$

This approximation, combined with a neglect of the right-hand side of Eq. (4.7), is known as the *adiabatic approximation.* This truncation of the BH expansion scheme is the only one that preserves the separability of nuclear and electron coordinates. The right-hand side of Eq. (47) represents the interaction with PES's defined by $E_e'(R)$ $(e' \neq e)$ giving rise, for example, to what is known as intersurface hopping in chemical dynamics.

At first sight it seems that the BH expansion represents an improvement over the BO treatment. No restrictive assumptions, equilibrium configuration R_0, or convergence of the perturbative type are needed. However, we are not getting something for nothing here, and that this is so, can be easily suspected by reminding the reader that both approaches use H_1 as the operator that "disturbs" the clamped-nuclear model for a molecule.

D. Practical application of BO and BH treatments–a critique

The BO analysis was mainly motivated to explain the observed ir and microwave spectroscopies, which can be associated with vibrational and rotational transitions of a semirigid molecule. It also had the agreeable effect of being consistent with the presupposed existence of a structure for such a molecule, and giving an operational definition of R_0. This supported the notion, firmly grounded in interpretations of many experiments of chemists, that molecules *have* structure. Therefore, insofar as each PES has well-defined, well-separated deep minima (leading to a satisfaction of all BO requirements), we can expect the BO treatment to be physically sound, and to provide good predictions.

Unfortunately that is not the way the PES concept is being used in many cases. Two examples follow:

(1) *Nonrigid molecules.*[9] The entire theory of such molecules is based on the assumed appropriateness of a single ground-state PES. Notwithstanding its obvious mathematical elegance and qualitative predictive power, it must be remembered that essentially none of the BO requirements are satisfied: the PES minima are shallow and there are many. Thus they are poorly separated, and the vibrational amplitudes are intrinsically large. It should therefore come as no surprise that quantitative aspects of the theory (rotation barriers, level splittings, etc.) need a parametrization often in poor agreement with other experiments.[9]

(2) *Chemical dynamics.*[10] I include in this field all phenomena that involve non-self-bound (or continuum) molecular states, such as traditional scattering, collisional or photon ionization and dissociation, as well as resonance phenomena. All these phenomena are characterized by the existence of either reagents or products, or both, in more or less highly excited bound or continuum states. (Here I skip questions with regard to the quantum-mechanical definitions of reagents and products, and whether such definitions have a place in quantum theory. I assume them to be identifiable in the conventional chemical sense.) Using the PES language, such systems are usually in rovibronic states with nuclear configurations far from the equilibrium one R_0 ("hot states"), or even on surfaces without any minima at all ("dissociative states"). Moreover, it is known that multidimensional excited PES's have very often conical intersections,[11,12] for which the BO treatment breaks down immediately. It seems totally inappropriate, or at least unreliable, to invoke the BO approximation in these phenomena.

It is possible to make a more quantitative statement about this breakdown. I reminded the reader in Sec. II B that for R away from R_0 the BO separability is impossible beyond zeroth order. So, since BO is used in chemical dynamics manifestly away from R_0 configurations, the error in wave functions and energies already appears to first order in κ. This is, of course, particularly true for PES's without any minima such as a dissociative PES. Furthermore, in conventional chemical dynamics, which is equivalent to nuclear dynamics on PES's, the cross sections, branching ratios, etc., are sensitively determined by the entire effective potential (minima, maxima, shapes, curvatures). Therefore errors in these scattering quantities can only become larger than suggested by the above analysis. I conclude that with $\kappa \sim 10^{-1}$, which is typical, errors of tens of percents can be expected to occur.

It is not possible to remedy this situation by going to the BH expansion. There are three reasons: 1. BO and BH use the same H_1 as the perturbation and coupling operator, respectively. 2. When the BO treatment breaks down, say, at the 10% level like in chemical dynamics, the BH expansion can simply converge slowly. To appreciate this possibility it is sufficient to recall the implications of Assumption 1. Assume there is an equilibrium configuration R_0, and that Ψ describes motions of the nuclei far from this configuration, as expressed by $R-R_0=kU\sim R_0$. Then the expansions for H_0 and H_1 [Eqs. (29) and (21)] will converge slowly. In fact, in view of Assumption 1, these expansions are questionable because κU is not a small quantity anymore. But then we can expect the expansions for E and Ψ [Eqs. (38) and (39)] to be poorly convergent. The result is the inadequacy of Eq. (41) to describe $\Psi(r,U)$. In other words, large non-BO terms are needed, implying slow convergence of the BH expansion. In cases of dissociative PES's the situation is even worse: no single R_0 can be found about which κU is small for nonzero $\Psi(r,U)$. 3. Even if the adiabatic approximation of Eq. (49) were used, thus saving the PES concept, we would benefit little, because

$$|C_{ee}| << |E_e| \tag{50}$$

and $C_{ee}(R)$ is only weakly dependent on R. As a result, $R_0^{\text{ad}}\simeq R_0$ with R_0^{ad} the extremum in the adiabatic PES according to Eq. (48). A separation of H like

$$H=H_0'+K_n' ,$$

where

$$H_0'=H_0+C_{ee},\quad K_n'=K_n+K_{nn}-C_{ee}$$

will not help either; it effectively shifts only the $E_e(R)$ values, and does not stop the breakdown of the BO separation.

We must conclude that the BH expansion most likely converges slowly when BO breaks down, displacing the problem to a nasty numerical one, and at the same time removing the conceptual niceties of the PES concept.

The spectroscopy of the bound states of the hydrogen molecule provides strong support for the BO and adiabatic approximations, but it also represents a special case. Long regarded as an archetypical example of chemical bonding, it is probably the most extensively and accurately studied molecule, experimentally as well as theoretically.[13] These studies have provided accurate values for bound state energies of electronic ground and many excited states. The rovibrational states associated with the $^1\Sigma^+$ electronic ground state have been particularly well investigated. The nonadiabatic corrections amount to only 5% of the adiabatic shift $C_{ee}(R)$. The reason is simple: only hydrogen has no inner shells, and therefore its lowest few PES's are energetically the most separated of all molecules, leading to small ratios of off-diagonal elements to the difference in diagonal elements in the BH matrix. Moreover, avoided crossings occur only for highly excited PES's. Nonetheless, the work of Dressler *et al.*[13] indicates that the density of closely lying, interacting PES's increases rapidly enough for vibronic energy shifts to become substantial fractions of differences in excitation energies. We must conclude that the hydrogen molecule cannot be regarded either as a perfect showcase for the usefulness of the PES concept, and that at best it must be viewed as a unique system.

E. Essén's view of a molecule

The BO (and adiabatic) separabilities are usually explained by emphasizing the sluggishness of the nuclear motion in comparison with that of electrons. Due to their small masses, electronic states are viewed to follow nuclear motion adiabatically, i.e., to undergo progressive deformations with nuclear displacements rather than transitions.[1,3] In turn, the nuclei experience the electrons like a gas, providing an effective interaction. This physical picture is tacitly assumed to hold for any configuration R.

There is immediately something wrong with this explanation: BO's analysis shows this interpretation of the wave function to be correct only through second order in κ for small nuclear displacements around the equilibrium configuration R_0. For other configurations the BO separation of electron and nuclear coordinates breaks down after the zeroth order. Therefore, not only is this separation of limited accuracy, it is qualitatively inferior for nonequilibrium configurations. Moreover, BO says nothing about dissociative states, which are heavily used in chemical dynamics. It seems that the so-called "adiabatic" separation is only an *interpretation* of a very limited result, the BO analysis, rather than a physical reality.

Essén,[6] in an interesting contribution to the debate over the relationship between molecular structure and quantum theory, argued in favor of the existence of a separation between "collective" and individual" motions in low-lying molecular bound states. This separation arises from the form of the Coulomb potential, and has nothing to do with the smallness of $(m/\overline{M})$. Because of the nuclear massiveness, collective motions are almost entirely atomlike, and individual ones are electronlike. I consider this a very important result, which can be seen as the physical motivation for the molecular coupled cluster method introduced in the next section. Therefore I will review Essén's analysis here, with emphasis on the key ideas and steps. For details I refer to Ref. 6.

The starting point is the virial theorem, applicable for bound states, with the form for Coulombic system

$$\langle K\rangle=-\tfrac{1}{2}\langle V\rangle . \tag{51}$$

This theorem shows that, at least for low-lying states, the potential energy dominates in the sense that $|\Psi|^2$, with Ψ the molecular state, must be large in regions of configuration space S_M where V has large negative values. Let us denote $\mathbf{r}_i$ for the position of any particle in the molecule ($\mathbf{r}_e$ for electrons and $\mathbf{r}_n$ for nuclei), then we can write (in atomic units)

$$V=\sum_{\substack{i,j\\(i<j)}}\frac{Q_iQ_j}{r_{ij}} , \tag{52}$$

with the definitions

$$Q_e=-1,\quad Q_n=Z_n , \tag{53}$$

$$r_{ij}=|\mathbf{r}_i-\mathbf{r}_j| . \tag{54}$$

The charge neutrality of the molecule demands that

$$\sum_i Q_i=0 . \tag{55}$$

The dimensionality of S_M is $3(N_e+N_n)$, with N_n the number of nuclei. We can thus state in addition that, due to the virial theorem, the most important terms in V should be those with maximum $|Q_iQ_j|$ and $Q_iQ_j<0$.

For atoms this consideration immediately leads to (atomic) shell formation and the separation of the center-of-mass (c.m.) motion, the latter motion being nearly equal to that of the nucleus. The mean-field methods of Hartree and Hartree-Fock bear out the consequences of the principle: the shells are quite well separated, and provide gradually a complete screening of the nuclear charge.

For molecules the only arrangement of the particles in S_M that makes the potential energy strongly negative is the one with Z_n electrons "around" each nucleus with charge Z_n. As a result, the picture of a molecule consisting of (essentially) neutral subsystems (atoms), weakly interacting (chemical bonds) in some spatial arrangement (molecular structure) emerges. Electrons in the individual subunits should behave similar to atoms, and these units should behave as composite particles. Notice that thus far no reference is made to electron or nuclear masses and their dynamics. To show how and where these masses play a role in "Essén's molecule," some formalism has to be developed.

The coordinates of any particle in the molecule can be written

$$\mathbf{r}_i=\mathbf{R}+\mathbf{r}^C_{\gamma(i)}+\mathbf{r}^I_i \ . \tag{56}$$

$\mathbf{R}$ is the *molecular* c.m. vector, and $\gamma(i)=\alpha$ if particle i belongs to the αth *composite* subsystem. Therefore $\mathbf{r}^C_\gamma$ is the c.m. vector of the subsystem γ relative to the molecular c.m. and $\mathbf{r}^I_i$ is the *internal* position of the particle i relative to the c.m. of the subsystem to which it belongs.

The vectors in Eq. (56) are not all independent; we can impose the constraints

$$\sum_{\gamma(i)=\alpha} m_i\mathbf{r}^I_i=0,\quad \alpha=1,2,\ldots,\mathcal{N} \tag{57}$$

$$\sum_{\alpha=1}^{\mathcal{N}} \mathcal{M}_\alpha\mathbf{r}^C_\alpha=0 \ , \tag{58}$$

where

$$\mathcal{M}_\alpha=\sum_{\gamma(i)=\alpha} m_i \ . \tag{59}$$

$\mathcal{N}$ is the number of subsystems, and m_i is the mass of particle i. The following relationship exists:

$$\sum_{\alpha=1}^{\mathcal{N}} \mathcal{M}_\alpha=\sum_{i=1}^{N} m_i,\quad N=N_e+N_n \ . \tag{60}$$

So far I made no use of the virial theorem. In particular, I left the value Q_α of the subsystem's charge unspecified,

$$Q_\alpha=\sum_{\gamma(i)=\alpha} Q_i \ . \tag{61}$$

I shall now assume the subsystems to be neutral, i.e., $Q_\alpha=0$. The potential energy V is expressible as

$$V=V_I+V_{CC} \ , \tag{62}$$

$$V_I=\sum_{\alpha=1}^{\mathcal{N}} V^I_\alpha,\quad V_{CC}=\sum_{\substack{\alpha,\beta\\(\alpha<\beta)}}^{\mathcal{N}} V^{CC}_{\alpha\beta} \ , \tag{63}$$

$$V^I_\alpha=\sum_{\substack{i,j\\(i<j)}}^{N}\frac{Q_iQ_j}{r_{ij}},\quad \gamma(i)=\gamma(j)=\alpha \tag{64}$$

$$V^{CC}_{\alpha\beta}=\sum_{\substack{\gamma(i)=\alpha\\ \gamma(j)=\beta}}^{N}\frac{Q_iQ_j}{r_{ij}} \ . \tag{65}$$

V^I_α are the internal energies of the composite subsystems, and $V^{CC}_{\alpha\beta}$ are interaction energies between these systems. A consequence of the "Essén principle" is that any rearrangement of the particles other than in neutral subsystems would increase the potential energy, as it would bring either electrons or nuclei closer together. In other words, the subsystems are somehow disconnected. That fact will make

$$V_{CC}\ll V_I \ . \tag{66}$$

Returning now to the dynamics of the Essén molecule, the Hamiltonian for the internal motion can be written[6]

$$H=K+V \ , \tag{67}$$

$$K=K_C+K_I \ , \tag{68}$$

$$K_C=\sum_{\alpha=1}^{\mathcal{N}} K^C_\alpha=\sum_{\alpha=1}^{\mathcal{N}}\frac{(\mathbf{p}^C_\alpha)^2}{2\mathcal{M}_\alpha} \ , \tag{69}$$

$$K_I=\sum_{\alpha=1}^{\mathcal{N}} K^I_\alpha=\sum_{\alpha=1}^{\mathcal{N}}\sum_{\gamma(i)=\alpha}^{N}\frac{(\mathbf{p}^I_i)^2}{2m_i} \ , \tag{70}$$

where $\mathbf{p}^C_\alpha$ and $\mathbf{p}^I_i$ are momenta related to $\mathbf{r}^C_\alpha$ and $\mathbf{r}^I_i$, respectively. Combining Eqs. (62) and (67)–(70) we can now express

$$H=\mathcal{H}+K_C=H_I+H_C \ , \tag{71}$$

where

$$\mathcal{H}=H_I+V_{CC} \ , \tag{72}$$

$$H_I=K_I+V_I,\quad H_C=K_C+V_{CC} \ . \tag{73}$$

Thus far our treatment has been classical. Let us now consider the quantum mechanical implementation. If the various coordinates on which the quantum-mechanical operators depend were independent, we would have separability of the form

$$\Psi=X_C\Phi_I \ , \tag{74}$$

with

$$\begin{aligned} H_I\Phi_I&=E_I\Phi_I \ ,\\ H_CX_C&=E_CX_C \ , \end{aligned} \tag{75}$$

where E_I and E_C would be individual and collective eigenenergies. Moreover, according to Eq. (72), because of the smallness of m/M, with m and M the electron and a nuclear mass, respectively, $\mathcal{H}$ would be almost the same as the clamped-nucleus Hamiltonian H_0 of Eq. (7); the main difference is that H_I contains nuclear kinetic energies and V_{CC} depends on distances between centers of mass, not between nuclei. [See Eq. (65).] In most cases these differences are negligible, and we can retrieve the BO-like separation. But we must recognize the origin, namely the virial theorem and *not* the smallness of (m/M), for the separation of individual and collective motion.

Unfortunately the coordinates in the quantities of Eqs. (71)–(73) are not independent, due to conditions (57) and (58). Therefore the kinetic energy operators K_C and K_I cannot be obtained by just replacing $\mathbf{p}_\alpha^C$ and $\mathbf{p}_i^I$ with gradients. The correct treatment is given in an appendix of Ref. 6. The separation as suggested by Eqs. (74) and (75) is shown by Essén to still exist approximately. The derivation is involved, and the reader is referred to Sec. 5 of Essén's paper[6] for details. A few observations are in order. First, no attention is paid to (anti)symmetry requirements for identical particles in the molecule leading to exchange terms in Ψ. These requirements would obviously clutter the picture, but it should not invalidate its physical content, namely, the approximate separation of individual and collective motions within a molecule. In fact, inasmuch as the individual states Φ_I can be expressed as products of (strongly separated) subsystems, by virtue of Eqs. (63) and (70), (anti)symmetrization of Ψ will lead to physically significant effects only for permutations among particles *within* the subsystems. (See also Sec. IV A.)

Second, it might seem that Essén's analysis holds only for atoms weakly interacting through van der Waals's forces. It is, of course, true that in such systems the neutral subunits are the nearly unaltered atoms, with interaction energies very small compared to atomic energies, or even their excitation energies. In covalent molecules the interaction (or bond) energies are fractions of excitation energies, and the atoms involved have largely lost their physical identities, especially as far as low-lying excitations are concerned. Yet, in many ways such molecules retain a "sum-of-atoms" character, which is most vividly displayed in their x ray determined charge density maps. But covalent molecules do represent a tenuous example of Essén's view.

Finally, it should be pointed out that the subunits need not be neutral. Because of the dynamic (rather than static) character of a bound molecular state, electrostatic considerations alone cannot explain the ionicity of bonds. Details of the eigenvalues and eigenstates of the internal (or individual) Hamiltonians $H_\alpha^I = K_\alpha^I + V_\alpha^I$ will determine the relative charges of the subsystems. It is easy to modify the above analysis for molecular ions; the same physical picture emerges as for neutral molecules.

Although the Essén molecule presents a compelling picture, it does not provide a workable formalism. The main problem is the existence of the constraints (57) and (58). In Sec. III I will show how the coupled-cluster method can be implemented to treat the electrons and nuclei on the same dynamical footing. The above problem is avoided, and a new physical picture appears reminiscent of (but distinct from) Essén's view.

III. THE MOLECULAR COUPLED-CLUSTER METHOD

A. Introductory remarks

The coupled-cluster method was formulated in 1958 by Coester[14] in response to the ongoing debate about the existence[15] and proofs[16,17] of the linked cluster theorem in many-body perturbation theory. Instead of the order-by-order inspection of Brueckner,[15] or the time dependent and diagrammatic formulations of Goldstone[16] and Hubbard,[17] Coester provided an extremely compact, complete, and convincing proof by induction. No time dependence or diagrams, with their subtle aspects such as the factorization theorem for energy denominators, are needed. In retrospect it is unfortunate (although understandable) that this proof was largely ignored or overlooked.

In Coester's theory the cluster operators figure centrally. If Φ denotes some (anti)symmetrized product of N one-particle states, then the CC representation of the exact stationary state function Ψ is given by[18]

$$\Psi = e^{T}\Phi \ , \qquad (76)$$

where

$$T = \sum_{k=1}^{N} T_k \ . \qquad (77)$$

T_k are cluster operators of order k, which describe the corrections beyond the independent-particle approximation to Ψ as provided by Φ. The character of these corrections can be appreciated by expanding the exponential in Eq. (76). Let us group terms in the following manner:

$$\Psi = \left[1 + T_2 + \tfrac{1}{2}T_2^2 + \frac{1}{3!}T_2^3 + \cdots \right] \Phi + \mathcal{R} \ , \qquad (78)$$

where $\mathcal{R}$ represents the terms arising from operators T_k in Eq. (77) other than T_2. If T_2 describes the correlation correction involving all single pairs of particles in Φ, then T_2^2, T_2^3, etc., describe the corrections involving two, three, etc., pairs of correlating particles. The factor $(1/n!)$ reflect the proper counting of distinct terms in Eq. (78). The "remainder" contains, of course, all the terms that involve cross products of T_k's, including the operators T_1, with now obvious interpretations. The orbitals in Φ can be chosen self-consistently such that $T_1 \equiv 0$. The operators T_k describe linked clusters of k particles in the sense that none can be written as the product of lower-order operators. This property carries the essence of the linked cluster theorem of many-body perturbation theory.[14,17]

The special magic of the CC method is its extremely rapid convergence in cluster order k: practice has shown that for widely different many-body systems, with pair interactions only, about 99% of the correlation energy can be obtained at the $T = T_2$ level. The remaining 1% is almost entirely accounted for by T_3. This has been found particularly for closed-shell nuclei,[19] atoms,[20,21] and molecules.[21] Even systems such as the electron gas model[22] and the Lipkin model[23] show the same trend, which are very different systems not exactly of the closed-shell type. First introduced to chemistry by Cizek[24] in 1966, the CC method has taken a strong hold of computational quantum chemistry, as evidenced, for example, by a recent review[25] (see also Ref. 21). I agree with a recent article that the CC method should be regarded as the single most successful and diverse many-body method known to date.[26]

Apart from its numerical success, the CC method has also a computational advantage over many-body calculations with density matrices or Green's functions. This advantage was pointed out in an excellent review article by Negele.[27] Not only is the CC approach superior in the economy of the number of independent continuous variables to be solved for, the method suggests the natural and systematic truncations for its practical implementation.

Last but not least, the physical content and properties of the CC method are very appealing. It offers the natural conceptually accessible hierarchy of corrections beyond the independent particle approximation Φ. Just as mean-field-like approximations can be characterized as (nonlinear) coupled orbital theories, so can the CC method be viewed as the coupled pairs plus triples plus, etc., corrections to such theories.[27] As I will show below, the CC equations are also nonlinear (of a low degree) in the cluster amplitudes. The coupling between the CC equations is very weak,[21] which reflects that T_2, T_3, etc., describe manifestly different physical effects. Since the energy is only determined directly by Φ and T_2 (assuming $T_1 \equiv 0$), it is understandable that the effect of T_3 on the energy can be as small as 1%, regardless of the nature of the microscopic pairwise interactions. For its use in scattering and chemically dissociative processes it is important to note that the CC theory is size consistent,[25] a property shared only with perturbation theory.[15–17] In short, this property means that the CC wave function and the associated energy separate correctly when two (or more) noninteracting systems are described. This behavior arises from the exponential form of the wave operator connecting Φ and Ψ. It is also responsible for the ability of the CC method to describe extensive properties such as crystal cohesive energies.

All applications to date have been made on systems with identical particles. (Because of the isospin symmetry relation between neutrons and protons, this is also true for nuclei.)[19] There are physical reasons that the CC method can be applied to systems of distinguishable particles, or sets of identical particles.[26] Indeed, encouraged by Essén's view of a molecule, and the success of the CC method for very diverse systems with pairwise interactions only, I propose to implement the method on molecules. This proposal will be the subject of Secs. III B and III C.

B. CC method for stationary molecular states

I will present the molecular coupled cluster (MCC) method for time-independent (or stationary) problems with a minimum of formalism. In particular, I will leave unspecified whether its implementation will be made in "first-quantized" (integro-differential) form or "second-quantized" (creation-annihilation) form.[21] Moreover, I will postpone all details about symmetry requirements; a few comments on this question are included in Sec. IV.

Central to a dynamic theory of a molecule is the proper elimination of the center-of-mass motion. In Appendix A I have shown how this can be achieved most conveniently by reduction of the quantum N-body problem to a $(N-1)$-body problem, with $N = N_e + N_n$. The potential-energy operator V is invariant to a transformation from laboratory-frame coordinates to a parallel system with origin at one of the particles. The kinetic energy operator K assumes quite a different form in the new coordinate system, giving rise to one- and two-body terms. However, the c.m. motion separates, and the internal Hamiltonian H can be expressed as[28,29]

$$H = L + W \ , \tag{79}$$

where

$$L = L_e + L_n \ , \tag{80}$$

$$W = W_{ee} + W_{en} + W_{nn} \ . \tag{81}$$

Furthermore, in Appendix C I have given the proof that the internal angular momentum is invariant to the above coordinate transformation. The significance of this result[28] will be discussed below.

Let us now assume that the reference state is given by an (anti)symmetrized product of one-electron functions ϕ_e and one-nucleus functions ϕ_n. Just like the atomic shell orbitals are centered on the atomic nucleus, so the functions ϕ_e and ϕ_n can describe shells with the origin of the particle chosen in the above transformation as centroid of these shell orbitals. For example, the reference state for the water molecule could consist of a (closed) shell structure for the ten electrons centered at the oxygen nucleus, and two protons occupying two shell orbitals ϕ_n, also centered at this nucleus. In fact, as shown in Appendix A, it is advantageous to choose the heaviest nucleus in any molecule as the centroid of this "molecular shell model." In view of Appendix C these shell orbitals can be assigned definite angular momenta, like in the atomic shell model. I will return to this point and show its numerical implications.

The cluster operators T_k are solutions to equations that are obtained from the Schrödinger equation for the state Ψ [Eq. (76)].

$$He^{T}\Phi = Ee^{T}\Phi \ , \tag{82}$$

while satisfying the strong orthogonality (SO) conditions. These conditions can be stated most compactly after introducing some auxiliary operators. The reference state projector P is defined by

$$P = |\Phi\rangle\langle\Phi| \ . \tag{83}$$

The SO projector

$$Q = 1 - P \tag{84}$$

can be expanded like

$$Q = \sum_{k=1}^{N-1} Q_k \ , \tag{85}$$

where Q_k is the projector onto the subspace of the orthogonal complement to Φ spanned by the complete set of k-particle excitations.[21] The SO conditions can now be expressed as

$$QT_k = Q_k T_k = T_k \ , \tag{86}$$

$$T_k P = T_k \ . \tag{87}$$

Equation (87) reflects the fact that T_k is defined with respect to Φ, and Eq. (86) expresses its k-particle correlation character and projection onto the orthogonal complement of Φ. These conditions are similar to the orthogonality requirements for the successive terms in perturbation theory. To apply the CC method to the above molecular shell model, I now suppose the following truncation scheme for the cluster operators:

$$T \simeq T_2 + T_3 \ , \tag{88}$$

$$T_2 = T_{ee} + T_{en} + T_{nn} \ , \tag{89}$$

$$T_e = T_{een} \ . \tag{90}$$

The terms in Eqs. (89) and (90) have obvious interpretations. T_{ee} describes the electron-electron correlations as in previous atomic and molecular applications. T_{en} describes electron-nucleus correlations. This term is particularly important for the description of inner shells of atomic nuclei occupying nuclear states ϕ_n in the molecular shell reference state Φ. T_{nn} describes the nucleus-nucleus correlation among nuclear functions ϕ_n. This term can be associated most closely with traditional molecular structure. Consider two nuclear functions ϕ_n and ϕ_n, describing, say, the two protons in the water molecule. Because of the considerable localization of the protons near a certain O-H distance, one expects ϕ_n and $\phi_{n'}$, to be quite "thin shell orbitals." Similarly, T_{nn} can be expected to peak quite sharply near an H-H distance corresponding to the equilibrium value, with O-H distances comparable to the "classical" O-H bond length. Therefore the combination $\{\phi_n, \phi_{n'}, T_{nn'}\}$ describes a triangular relationship among the three nuclei, with the oxygen nucleus at the apex. In fact, one can imagine this relationship becoming quite rigid for very large nuclear masses, giving rise to the well-known semirigid (classical) molecular structure. Of course, this picture of an emerging structure from the molecular shell model can be extended to any number of nuclei. The above triads of two ϕ_n's and one $T_{nn'}$ will provide interlocking triangles which, in accordance with a well-known engineering principle, can give a perfectly rigid structure.

I believe that a T_3 operator of the T_{een} type [Eq. (90)] is necessary in the molecular shell model. This operator describes the correlation of two electrons in the vicinity of a nucleus. In view of Essén's molecule, this operator is important for describing the electron correlation within the neutral subsystems which are of atomic character. It should be viewed on the same footing as T_{ee}, which describes the electron pair correlation in the presence of the nucleus at the origin of the shell structure described by Φ. Application of my model to the H_2 molecule would also require a T_{een} operator, if not only on symmetry grounds, when using one proton as the shell structure centroid. Indeed, the best H_2 calculations, although variational, contain terms generated by such an operator.[13]

To obtain the equations for T_k we return to Eq. (82). Following Coester,[14] we first premultiply with $\exp(-T)$, and obtain

$$e^{-T} H e^{T} \Phi = E\Phi \ . \tag{91}$$

We observe

$$e^{-T} H e^{T} = H + [H,T] + \tfrac{1}{2}[[H,T],T] + \cdots \ . \tag{92}$$

Due to the SO conditions (86) and (87) and thanks to the presence in H of one- and two-body terms only, this commutator series truncates exactly after five terms. Since we can write for Q_k

$$Q_1 = Q_e + Q_n \ , \tag{93}$$

$$Q_2 = Q_{ee} + Q_{en} + Q_{nn} \ , \tag{94}$$

etc., with obvious meaning of the subscripts, the CC equations for the truncations (88)–(90) can be obtained by projection of Eq. (91).

$$E = \langle \Phi \,|\, H + HT_2 \,|\, \Phi \rangle \ , \tag{95}$$

$$Q_1 e^{-T} H e^{T} \,|\, \Phi \rangle = 0 \ , \tag{96}$$

$$Q_2 e^{-T} H e^{T} \,|\, \Phi \rangle = 0 \ , \tag{97}$$

$$Q_{een} e^{-T} H e^{T} \,|\, \Phi \rangle = 0 \ . \tag{98}$$

Equation (95) reflects the property that the energy is only determined by the orbitals ϕ_e and ϕ_n, and T_2. Equation (96) gives the mean-field-like equations for the orbitals ϕ_e and ϕ_n.[27] In fact, because of (93) it really consists of two sets of equations. Similarly, Eq. (97) represents three sets of equations. Equations (96)–(98) provide a number of equations equal to that of unknown quantities. Of course, these equations hide a considerable proliferation of terms. For example, the energy expression expands to

$$\begin{aligned} E = {} & \langle \Phi \,|\, L_e + W_{en} + W_{ee} + W_{en} T_{en} + W_{ee} T_{ee} \,|\, \Phi \rangle \\ & + \langle \Phi \,|\, L_n + W_{nn} + W_{nn} T_{nn} \,|\, \Phi \rangle \ . \end{aligned} \tag{99}$$

Equation (96) expands to

$$Q_1 (H + [H,T_2] + [W,T_3]) \,|\, \Phi \rangle = 0 \ . \tag{100}$$

A further expansion occurs in view of Eq. (93):

$$\begin{aligned} & Q_e (L_e + W_{ee} + W_{ne} + [L_e, T_{ee}] + [L_n, T_{en}] \\ & \quad + [W_{ee}, T_{ee}] + [W_{en}, T_{en}] + [W_{en}, T_{een}]) \,|\, \Phi \rangle = 0 \ , \end{aligned} \tag{101}$$

$$\begin{aligned} & Q_n (L_n + W_{nn} + W_{en} + [L_n, T_{nn}] + [L_e, T_{en}] \\ & \quad + [W_{nn}, T_{nn}] + [W_{en}, T_{en}] + [W_{ee}, T_{een}]) \,|\, \Phi \rangle = 0 \ . \end{aligned} \tag{102}$$

Equation (99) has been written in a form that displays the separation in manifest electronic and nuclear terms, and in an order of suspected decreasing magnitudes. Equations (101) and (102) are Brueckner-Hartree-Fock (BHF) equations[30] (reducing to Hartree-Fock equations when $T_2 = T_3 = 0$) which provide the equations for ϕ_e and ϕ_n. Somewhat expanded forms for Eqs. (97) and (98) are

$$Q_2 (H + [H,T_2] + \tfrac{1}{2}[[W,T_2],T_2] + [W,T_3]) \,|\, \Phi \rangle = 0 \ , \tag{103}$$

$$\begin{aligned} & Q_{een} ([W,T_2] + [H,T_3] + \tfrac{1}{2}[[W,T_2],T_2] \\ & \quad + [[W,T_2],T_3]) \,|\, \Phi \rangle = 0 \ . \end{aligned} \tag{104}$$

For the last term in Eq. (104) I have used the commutation of T_2 and T_3 due to Eqs. (86) and (87). The reader can easily convince himself that Eqs. (101) and (102) provide cubic equations in $\{\phi_e\}$ and $\{\phi_n\}$, like HF equations, whereas Eqs. (103) and (104) are quadratic in T_2 and linear in T_3, respectively. It is quite probable that several terms in these equations are negligible either on purely numerical or on physical grounds; I defer an analysis of this possibility to later publications. Finally, since only T_{een} is kept, a considerable reduction of terms in Eq. (104) occurs compared to the situation with T_{eee} and/or T_{nnn} included.

C. CC method for time-dependent molecular states

In 1977 I formulated a CC approach to the calculation of static and dynamic properties.[31] Recent applications have shown the efficacy of this formulation.[32] Dynamic properties require the CC solution to the time-dependent Schrödinger equation due to the adiabatic turn-on of an external electromagnetic field perturbation. This time-dependent CC theory can, however, also be used for bound nonstationary states as well as any continuum states describable with the time evolution of a many-particle wave packet, and with or without a time-dependent Hamiltonian H. Negele[27] took this approach for the microscopic underpinning (and improvement) of the time-dependent Hartree-Fock (TDHF) method for nuclear scattering. I propose to do the same for molecular states with nonseparable time dependence. I am confident of its success for the same physical arguments as used by Negele,[27] as well as an additional one.

The starting point is the time-dependent Schrödinger equation in CC form, expressible as [see Eq. (91)] (in atomic units)

$$e^{-T}He^{T}\Phi = ie^{-T}\frac{\partial}{\partial t}e^{T}\Phi \ . \tag{105}$$

We assume all quantities in Eq. (105) to be time dependent, including the ϕ_e and ϕ_n making up Φ. Writing

$$\dot{T} = \partial T/\partial t \ , \tag{106}$$

with T satisfying the SO conditions in time-dependent form (P and Q are time-dependent projection operators because of the time dependence of ϕ_e and ϕ_n), we can expand[33] (note that $[\partial/\partial t, T] = T$)

$$e^{-T}\frac{\partial}{\partial t}e^{T} = \frac{\partial}{\partial t} + \dot{T} + \tfrac{1}{2}[\dot{T},T] \ . \tag{107}$$

Multiple commutations vanish because of the SO conditions of Eqs. (86) and (87); this can be easily proven by recognizing the relations

$$\frac{\partial}{\partial t}|\phi_e\rangle = \sum_{\epsilon} |\phi_\epsilon\rangle\langle\phi_\epsilon|\dot{\phi}_e\rangle \ , \tag{108}$$

$$\frac{\partial}{\partial t}|\phi_n\rangle = \sum_{\nu} |\phi_\nu\rangle\langle\phi_\nu|\dot{\phi}_n\rangle \ , \tag{109}$$

where $\{\phi_\epsilon\}$ and $\{\phi_\nu\}$ are the complete sets of electron and nuclear states, including the occupied $\{\phi_e\}$ and $\{\phi_n\}$ used to define P and Q_k.

We now make the important assumption that *for time-dependent cluster functions $T_k(t)$ describing nonseparable time-dependent molecular states, the truncations*

$$T(t) \simeq T_2(t) + T_3(t) \ , \tag{110}$$

$$T_2(t) = T_{ee}(t) + T_{en}(t) + T_{nn}(t) \ , \tag{111}$$

$$T_3(t) = T_{een}(t) \ , \tag{112}$$

are at least as appropriate as for the stationary states. I base this assumption on the facts that we have

$$\langle \Psi(t) \,|\, \Psi(t) \rangle < \infty \ , \tag{113}$$

and that "Essén's view" of a molecule need not necessarily be time independent. Because the virial theorem need not hold anymore, one can expect any structural content of $\Psi(t)$ expressed in CC form to be at least less than that for stationary states. In fact, there exists the obvious inequality

$$\left| \frac{\langle K \rangle(t)}{\langle V \rangle(t)} \right| \geq \tfrac{1}{2}, \quad \langle V \rangle < 0 \ , \tag{114}$$

with expectation values taken with respect to $\Psi(t)$. This inequality holds because for scattering states the internal kinetic energy can exceed beyond any limits. This causes the particles to become more randomly distributed and thus remain, on the average, at ever larger distances from each other, leading to a decrease in $|\langle V \rangle|$. If the kinetic energy becomes comparable to the potential energy or even exceeds it, the tendency towards "crystallization" into an Essén-like structure diminishes and a mean-field-like description of $\Psi(t)$ can suffice. The conclusion is forced on us that T_2 and T_3 will be *less* important for a more energetic molecular state, i.e., the larger $\langle H \rangle(t)$ becomes. As a corollary, we can expect the CC expansion for $\Psi(t)$ to converge even better than for stationary states, a surprising possibility indeed.

Projecting Eq. (105) against P and Q_k, and using Eq. (107) we obtain

$$Pe^{-T}He^{T}|\Phi\rangle = iP\left[\frac{\partial}{\partial t} + \dot{T} + \tfrac{1}{2}[\dot{T},T]\right]|\Phi\rangle \ , \tag{115}$$

$$Q_1 e^{-T}He^{T}|\Phi\rangle = iQ_1\left[\frac{\partial}{\partial t} + \dot{T} + \tfrac{1}{2}[\dot{T},T]\right]|\Phi\rangle \ , \tag{116}$$

$$Q_2 e^{-T}He^{T}|\Phi\rangle = iQ_2\left[\frac{\partial}{\partial t} + \dot{T} + \tfrac{1}{2}[\dot{T},T]\right]|\Phi\rangle \ , \tag{117}$$

$$Q_{een} e^{-T}He^{T}|\Phi\rangle = iQ_{een}\left[\frac{\partial}{\partial t} + \dot{T} + \tfrac{1}{2}[\dot{T},T]\right]|\Phi\rangle \ . \tag{118}$$

As discussed in Ref. 27, Eq. (115) is devoid of any physical content for time evolution; it is satisfied identically only when all clusters of Eq. (77) are included. Equation (116) provides the time-dependent equations for ϕ_e and ϕ_n, similar to Eq. (96). When $T_2 = T_3 = 0$, these equations reduce to the TDHF equations.[27] This connection is very important for formal as well as computational reasons.

The structure of the right-hand sides of Eqs. (116)–(118) is very attractive computationally.[27] The solution of the equations will proceed numerically in time. At any time t the functions ϕ_e and ϕ_n, as well as their time derivatives and $T_2(t)$ and $T_3(t)$ will be known. Therefore, Eqs. (117) and (118) provide first-order differential equations in the cluster functions (or amplitudes) associated with T_2 and T_3. It is then straightforward, at least in principle, to obtain all the CC quantities at time $(t+\Delta t)$.

The choice of the initial conditions for my time-dependent MCC model is nontrivial, and is similar to that in the TDHF method.[27] No universal prescription can be given, as it crucially depends on the physics of the system and the measurement process that one wishes to describe. Discussion of this point will be covered in future publications.

IV. FUTURE PROGRAM

In this section I would like to bring together the most important questions that need to be addressed before the MCC method can be brought to full bloom. These questions are in order of priority as presently perceived.

A. Symmetry and conservation laws

For the time-independent MCC method I proposed the use of shell orbitals with definite angular momenta. This choice will be advantageous to obtain MCC states of definite total angular momentum, similar to the situation in atoms; the result of Appendix C makes this possible. But this enables us to implement mixed analytic-numerical techniques developed for atomic CC calculations as explained in Ref. 20. Of course, due to different localization of ϕ_n and cluster functions involving nuclei, a different numerical integration scheme will be needed. However, the reduction to one- and two-dimensional differential equations will still be possible.

It is important to recall that my proposal does *not* contain a zeroth-order starting point; the orbitals ϕ_e and ϕ_n are uniquely defined (up to unitary transformations) as solutions to BHF-type equations.[30] Therefore treatment of open-shell systems (with respect to electrons, that is) might present novel possibilities. In particular, the use of multideterminantal (or multi-Φ) reference states might be avoided.

Proper treatment of spin symmetry needs careful attention. This symmetry is closely related with permutation symmetry among identical half-spin particles, provided H does not contain spin-dependent operators. We showed the spin-free character of T_k for closed-shell electronic systems.[21]

This brings us directly to the question of the correct recognition of the operators comprising the complete group of the Hamiltonian H. A lucid discussion of this question, and its significance to molecular spectroscopy, particularly of nonrigid molecules, was given by Longuet-Higgins.[33,34] (See also Ref. 9.) He introduced the concept of feasible versus unfeasible transformations induced by elements of the above group. Feasible transformations among identical nuclei are those that "can be achieved without passing over an insuperable energy barrier" (on a ground PES).[34] Such transformations give rise to energy splittings that are experimentally observable. A classic example is the "inversion transformation" in the ammonia molecule giving rise to its MASER action. Unfeasible transformations, which lead to no observable splitting, require the "breaking and making of bonds."[9,34] The practical effect is that for spectroscopic purposes one can restrict consideration to the subgroup of the complete group of H consisting of the feasible operations (permutations, inversion, and their products) only.

The notion of feasibility of symmetry operations can be extended to electrons. For example, permutations among valence electrons are clearly feasible, as they give rise to splittings and/or shifts in orbital energy levels in, say, HF calculations. But similar operations among core orbitals on different atoms must be considered unfeasible: such orbitals have negligible overlap. In quantum chemical terms we state that such core states have negligible exchange interaction, and we should be able to ignore such permutations from the totally symmetric group. It would be very valuable to exploit the concept of unfeasible operations for electrons as well as nuclei, since it can substantially reduce the computational effort without impairing the physical relevance of the calculations.

At present we do not know which symmetries of the complete group of H will be consistent with the cluster truncation scheme I propose. This is an important question because the answer will determine which "theoretical resolution" of stationary state quantum numbers will be possible. This will determine the relevance of the MCC method for high-resolution spectroscopies.

Negele[27] showed the existence of conservation laws for the TDHF method, such as those for energy, angular momentum, and linear momentum. It is important to establish similar conservation laws for the time-dependent MCC method.

B. Approximations, simplifications, and computational considerations

I pointed out in Sec. IV A that the MCC equations contain many terms; the slightly expanded forms (101)–(114) are just a glimpse. Yet it is known from practical experience that not all terms are of the same magnitude[21] and that partial cancellations occur.[25] Similar findings can be expected in the MCC method. The experiences with electron correlation calculations will almost certainly carry over; there seems to be not much change in the electronic wave function. This was shown in Hartree-Fock-like calculations that include nuclear dynamics in intriguing work by Thomas.[35] To the extent that the coupling between electron and nuclear dynamics is weak, we can expect some terms that describe this effect to be relatively small, perhaps negligible. This could be particularly relevant in Eqs. (103) and (117). Both physical and numerical arguments will be needed to identify reliable approximations.

Simplifications can occur once we have understood the symmetry and other group theoretical properties of the

MCC method. For example, we could find a way to eliminate spin from all or some of the cluster operators, as in our earlier work on electron correlation.[21] On the other hand, we would be hampered in generality of our method if too many symmetries are "built into" our working equations.

All the above considerations apply to the time-dependent as well as time-independent MCC method. This is evident from the equivalence of the left-hand sides of Eqs. (96)–(98) and (116)–(118), as well as the observations with regard to the convergence of the CC expansion for $\Psi(t)$.

Computational questions need to be addressed. It would be preferable to use a first-quantized basis-set independent representation which has proven so successful in electron correlation calculations,[21,36–38] thanks to the use of explicitly correlated Gaussian geminal expansions. For stationary states the molecular shell structure can be invoked which makes the use of centrosymmetry possible.[20] For time-dependent calculations that possibility will depend on the initial conditions and/or the nature of the external perturbation, in which case either fully numerical[39] or Gaussian geminal approaches are needed.

C. Properties and excited states

My approach to the evaluation of static and dynamic properties, formulated with only electrons in mind,[31,32] can of course be used with the MCC model as the starting point. Introducing an external perturbation to the molecular Hamiltonian

$$H \to H(\lambda) = H + \lambda H' , \tag{119}$$

where H' represents a static or dynamic (i.e., time-dependent) coupling to the external probe, order-by-order calculation of properties proceeds as in Ref. 28. If the cluster operators are expanded like

$$T(\lambda) = T + \lambda T^{(1)} + \frac{\lambda^2}{2} T^{(2)} + \cdots , \tag{120}$$

then the various orders of properties can be extracted from the perturbative expansion of the energy (λ):

$$E(\lambda) = E + \lambda E^{(1)}\{T^{(1)}\} + \frac{\lambda^2}{2} E^{(2)}\{T^{(1)}, T^{(2)}\} + \cdots . \tag{121}$$

The $E^{(r)}$ are dependent on $T^{(1)}$ to $T^{(r)}$, and each $T^{(k)}$ is the solution to an inhomogeneous linear equation with the inhomogeneous term depending on $T, T^{(1)}, \ldots, T^{(k-1)}$. This structure of the equations assures an accurate evaluation of properties, provided that good basis sets are chosen. The orbitals ϕ_e and ϕ_n as well as T_k are kept fixed in the replacement (119). Therefore, with H' a one-particle coupling operator (which is usually the case), we expect (see also Ref. 40)

$$T^{(r)} \simeq T_1^{(r)} + T_2^{(r)} , \tag{122}$$

with obvious notation. If a first-quantized formulation of the MCC method succeeds, then a similar truncation should be used for $T^{(r)}$.

Excitation energies and transition probabilities can be obtained with time-dependent H'; I refer to Dalgaard and Monkhorst[31] for a discussion of the relationship with Green's function-based dynamic response functions. The same considerations with regard to structure of equations and basis functions apply to these quantities as well.[32,40] If $H'(t)$ is also a one-particle operator, we expect a truncation such as Eq. (122) to be adequate.

With the introduction of the time-dependent MCC method, which so far was formulated with a time-independent internal Hamiltonian H, the exciting possibility arises to combine it with the presence of an external time-dependent perturbation. Examples are laser pulse probes and molecular passage through an intense electromagnetic field,[41] both of which can be described with a characteristic shape (in time) for H'. One can imagine the molecule to be in a stationary state before H' is turned on at $t=0$, which will define the initial state of $\Psi(t)$ (at $t=0$). For $t>0$ the molecular Hamiltonian will be

$$H(t) = H + H'(t) \tag{123}$$

for the duration τ of the external probe, after which the molecular Hamiltonian again becomes H. Continuation of the time evolution numerically will reveal the consequences of the probing: dissociation, ionization, excitation, or creation of a mixture of stationary states. Recent studies of "half collisions" also belong to this class of phenomena. These consequences can be identified by monitoring the time evolution of all CC quantities, i.e., ϕ_e, ϕ_n, T_2, and T_{een}. In any case, the time-dependent MCC method could provide a powerful tool for understanding laser chemistry, and picosecond and femtosecond spectroscopy.

D. Relationship to potential-energy surfaces

As pointed out, the concept of a PES is intimately connected with the BO approximation; it arises as a purely electronic eigenvalue by suppressing the nuclear kinetic energy operator H_1 [see Eqs. (19) and (28)]. In the MCC method the electronic and nuclear kinetic energy operators are treated at the same footing. In fact, as evidenced in Eqs. (101) and (102), the electronic and nuclear orbital equations contain both these operators [the two- and three-body equations (103) and (104) contain electron-nucleus mass polarization terms as well, which provide additional dynamic coupling]. Therefore a PES does not emerge naturally in the MCC method.

If one still wishes to extract a PES, an ambiguity of its definition has to be admitted. On the one hand, the MCC method is not variational, and therefore an expectation value-like expression such as

$$E_e^{\mathrm{NA}}(R) = \frac{\langle \Psi | H_0 | \Psi \rangle_r}{\langle \Psi | \Psi \rangle_r} , \tag{124}$$

with Ψ the MCC wave function and integration over electronic coordinates r only, is not very consistent with the theory. This form of a nonadiabatic (NA) PES was advocated by Wilson.[42] On the other hand, its outstanding virtue is that this definition coincides with the BO form if Ψ is a BO wave function.[42] It should also be pointed out that the variational and MCC forms of the energy coincide for untruncated cluster expansions in Eq. (77).[43,44] This fact makes Eq. (124) even more plausible.

The dependence of $E_e^{\text{NA}}(R)$ on R is difficult to see. Since the integration is over r only, this quantity is not obviously representable as a sum of linked terms.[44] Yet it seems that a PES can be represented as a sum of linked terms depending on one, two, three, etc., nuclear coordinates in a nonseparable manner.[2] With Ψ in the BO approximation and Ψ_e expressed in coupled-cluster form, it is easy to show that $E_e(R)$ consists of linked diagrams only.[42,44] A proof that this is also the case with Ψ in MCC form would be desirable.

However, it is evident from Eq. (124) that $E_e^{\text{NA}}(R)$ will contain high-order cluster terms when expanded in internuclear coordinates. This is due to the exponential form of the operator connecting Φ to Ψ, even with our truncation after T_3. The same holds at the BO approximation level.[44] We may therefore expect that E_e^{NA} is also a function of R expressible as a linked cluster expansion through N_nth order with N_n the number of nuclei.

V. SUMMARY AND CONCLUSION

I have revisited the Born-Oppenheimer approximation and the Born-Huang expansion for the description of molecular eigenstates. Due to the violation of several requirements for the applicability of the BO-like separation of electronic and nuclear coordinates, serious and persistent errors can be expected in many applications. The most significant requirement is the existence of a nuclear localization around an equilibrium configuration R_0, i.e., a deep minimum in the PES. Notable applications of BO which ignore this condition are nonrigid molecule dynamics and chemical dynamics. Since the BO analysis breaks down in these cases after zeroth order in the BO mass parameter, errors in the order of 10% should be no surprise. The BH expansion provides no solace, since I showed it to converge poorly when BO fails.

Inspired by an alternative view of a molecule due to Essén, I proposed the implementation of the coupled-cluster method for both the electrons and nuclei of the molecule. This led logically to a formulation of the molecular coupled-cluster method, both in time-independent and time-dependent forms. The first version is appropriate for calculating stationary states, whereas the second one is applicable for any time-dependent square-integrable many-particle wave-packet state for which initial conditions can be specified. Much work is needed to implement the MCC method, but the quantum physics seems to be well understood.

The range of applicability is only bounded by practical limitations; I believe the CC truncation scheme to be valid for any size molecule. But, of course, computations will become quickly prohibitive for larger molecules. I imagine the MCC method to find its first serious applications in high-resolution spectroscopies and chemical dynamics involving no more than five- to ten-atom molecules, if that large. Therefore I do not foresee the quick demise of the BO approximation, if not only because old ideas die hard. But doubts and debates about its legitimacy continue as evidenced by recent publications by Grelland and Woolley.[45]

ACKNOWLEDGMENTS

I am grateful for the open-ended hospitality extended to me by my colleagues and friends at the Institute "Rudjer Bosković." In particular I wish to mention Dr. S. Bosanac, Dr. A. Graovac, Dr. Z. Maksić, Dr. Z. Meic, Dr. Z. Veksli, and Dr. A. Velenik, who all in their special personal ways contributed to the realization of this paper. I also wish to thank Dr. G. Ezra, Dr. W. A. Lester, Dr. C. Obcemea, and Dr. L. Stolarczyk, for critical readings and comments. This work was supported in part by National Science Foundation Grant No. CHE-850733.

APPENDIX A: THE INTERNAL MOLECULAR HAMILTONIAN

The elimination of the center-of-mass motion from the molecular Hamiltonian is necessary because of the interest for the dynamics of the internal degrees of freedom, rather than that of the system in motion, which has a continuous spectrum of eigenenergies. Since the potential energy for a molecule V is a function of interparticle distances only (at least in the absence of external fields, which might cause anisotropies), it is invariant to any coordinate transformation. Therefore, we need only consider the molecular kinetic energy operator K_M when introducing some transformation to affect the c.m. separation.

Several possibilities exist to achieve this separation. All of them at least use the c.m. vector $\mathbf{R}$ defined as

$$\mathbf{R}=\frac{1}{M}\sum_{i=1}^{N} m_i\mathbf{q}_i\ , \tag{A1}$$

with

$$M=\sum_{i=1}^{N} m_i\ , \tag{A2}$$

the total mass of the molecule, and $\mathbf{q}_i$ the position vectors of the particles as measured in the laboratory frame (LF) considered as an inertial frame. Other coordinates sometimes chosen are hyperspherical coordinates or coordinates relative to the c.m.,

$$\rho_i=\mathbf{q}_i-\mathbf{R}\quad (i=1,\ldots,N-1)\ , \tag{A3}$$

$$\rho_N=-\frac{1}{m_N}\sum_{i=1}^{N-1} m_i\rho_i\ . \tag{A4}$$

A disadvantage of this coordinate system is the linear dependence of $(\rho_1,\ldots,\rho_N)$, because of (A4). This causes problems similar to those discussed by Essén[6] in his appendix. Another choice is the set of coordinates relative to the center-of-mass for the nuclei.[46] But now linear dependence occurs among nuclear coordinates, leading to an awkward dependence of V on these coordinates. (Diatomic molecules are an exception.) We can only avoid these problems by introducing the independent set of coordinates[28,29]

$$\mathbf{r}_i=\mathbf{q}_i-\mathbf{q}_N\quad (i=1,\ldots,N-1)\ , \tag{A5}$$

and the c.m. vector $\mathbf{R}$. Since we can write

$$K_M = -\hbar^2 \sum_i \frac{\Delta_i}{2m_i} = -\sum_i \frac{\hbar^2}{2m_i}(\partial/\partial \mathbf{q}_i)^2 , \tag{A6}$$

and

$$\partial/\partial \mathbf{q}_i = \sum_{j=1}^{N-1} \frac{\partial \mathbf{r}_j}{\partial \mathbf{q}_i} \partial/\partial \mathbf{r}_j + \frac{\partial \mathbf{R}}{\partial \mathbf{q}_i} \partial/\partial \mathbf{R} , \tag{A7}$$

we quickly obtain the results

$$\partial/\partial \mathbf{q}_i = \partial/\partial \mathbf{r}_i + \frac{m_i}{M}\partial/\partial \mathbf{R}, \quad i < N \tag{A8}$$

$$\partial/\partial \mathbf{q}_N = -\sum_{j=1}^{N-1} \partial/\partial \mathbf{r}_j + \frac{m_N}{M}\partial/\partial \mathbf{R}, \quad i = N . \tag{A9}$$

Substituting (A8) and (A9) in (A6) we get

$$K_M = K_{\mathrm{c.m.}} + \sum_{i=1}^{N-1} K_i + \sum_{\substack{i,j \\ (i<j)}}^{N-1} K_{ij} , \tag{A10}$$

$$K_{\mathrm{c.m.}} = -\frac{\hbar^2}{2M}(\partial/\partial \mathbf{R})^2 , \tag{A11}$$

$$K_i = -\sum_{i=1}^{N-1} \frac{\hbar^2}{2\mu_i}(\partial/\partial \mathbf{r}_i)^2 , \tag{A12}$$

$$K_{ij} = -\frac{\hbar^2}{m_N}(\partial/\partial \mathbf{r}_i)(\partial/\partial \mathbf{r}_j) , \tag{A13}$$

where

$$\mu_i^{-1} = m_i^{-1} + m_N^{-1} . \tag{A14}$$

We can now write the internal Hamiltonian H as

$$H = L + W , \tag{A15}$$

with

$$L = \sum_{i=1}^{N-1} L_i , \tag{A16}$$

$$L_i = K_i + V_{iN} , \tag{A17}$$

$$W = \sum_{\substack{i,j \\ (i<j)}}^{N-1} W_{ij} , \tag{A18}$$

$$W_{ij} = V_{ij} + K_{ij} . \tag{A19}$$

The transformation (A5) is to a noninertial frame of reference, centered at $\mathbf{q}_N$; the "velocity-dependent" potentials K_{ij} are a consequence of such frame. In order to minimize the effect of these potentials we should choose $\mathbf{q}_N$ as the coordinates of the heaviest nucleus, since on the average, the c.m. will be closest to that point.

It is important to observe that for neutral molecules

$$\sum_{i=1}^{N-1} Q_i = -Q_N , \tag{A20}$$

with Q_i defined by Eq. (53). This will cause each shell orbital to be determined by attractive potentials, at least for asymptotically large distances from $\mathbf{q}_N$.

APPENDIX B: SOLUBILITY CONDITIONS IN THE BO ANALYSIS

The solution of perturbation equations always proceeds hierarchically: higher-order equations can only be solved after lower-order solutions have been obtained. Usually the zeroth-order equation is homogeneous in the zeroth-order wave function, whereas all other equations can be cast in the form of linear inhomogeneous equations. Imposition of proper physical boundary conditions will lead to unique solutions to the zeroth-order equation only if no degeneracy occurs. The other inhomogeneous equations have solutions only if the inhomogeneous part is orthogonal to the homogeneous solution with respect to the proper variable. This requirement leads to so-called solubility conditions.

The BO analysis gives rise to a similar situation, but with two unique twists: the molecular Hamiltonian is also expanded in an infinite series, and we encounter two sequences of perturbation equations. These sequences are connected with the solution of the clamped-nucleus electronic Schrödinger. The former sequence is solved independently, whereas the latter one can only be solved with the solutions of the former.

We found [see Eqs. (19)–(24) and (29)] that the Hamiltonian H can be expanded like

$$H = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2 (H_0^{(2)} + H_1^{(2)}) + \kappa^3 (H_0^{(3)} + H_1^{(3)}) + \cdots . \tag{B1}$$

The operators $H_0^{(r)}$ are homogeneous functions of the nuclear displacement coordinate U [see Eqs. (29)–(31)]; they arise in the order-by-order solution of the clamped-nucleus electronic Schrödinger problem

$$[H_0 - E_e(R)]\Psi_e(r,R) = 0 , \tag{B2}$$

with expansions

$$H_0 = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2 H_0^{(2)} + \kappa^3 H_0^{(3)} + \cdots , \tag{B3}$$

$$E_e(R_0 + \kappa U) = E_e^{(0)} + \kappa E_e^{(1)} + \kappa^2 E_e^{(2)} + \cdots , \tag{B4}$$

$$\Psi_e(r, R_0 + \kappa U) = \Psi_e^{(0)} + \kappa \Psi_e^{(1)} + \kappa^2 \Psi_e^{(2)} + \cdots , \tag{B5}$$

$E_e^{(r)}$ and $\Psi_e^{(r)}$ are homogeneous in U of the rth degree. Equating coefficients of different powers of κ to zero gives the first sequence of perturbation equations:

$$(H_0^{(0)} - E_e^{(0)})\Psi_e^{(0)} = 0 , \tag{B6}$$

$$(H_0^{(0)} - E_e^{(0)})\Psi_e^{(1)} = -(H_0^{(1)} - E_e^{(1)})\Psi_e^{(0)} , \tag{B7}$$

$$(H_0^{(0)} - E_e^{(0)})\Psi_e^{(2)} = -(H_0^{(1)} - E_e^{(1)})\Psi_e^{(1)} - (H_0^{(2)} - E_e^{(2)})\Psi_e^{(0)} , \tag{B8}$$

etc. We consider this sequence to be solved.

The second sequence of perturbation equations arises from the full molecular Schrödinger equations

$$(H - E)\Psi(r,R) = 0 . \tag{B9}$$

H is expanded according to Eq. (B1) and E and Ψ are expanded like

$$E = E^{(0)} + \kappa E^{(1)} + \kappa^2 E^{(2)} + \cdots , \tag{B10}$$

$$\Psi=\Psi^{(0)}+\kappa\Psi^{(1)}+\kappa^2\Psi^{(2)}+\cdots . \tag{B11}$$

Notice that $E^{(r)}$ are constants. The order-by-order equations are

$$(H_0^{(0)}-E^{(0)})\Psi^{(0)}=0 , \tag{B12}$$

$$(H_0^{(0)}-E^{(0)})\Psi^{(1)}=-(H_0^{(1)}-E^{(1)})\Psi^{(0)} , \tag{B13}$$

$$(H_0^{(0)}-E^{(0)})\Psi^{(2)}=-(H_0^{(1)}-E^{(1)})\Psi^{(1)} -(H_0^{(2)}+H_1^{(2)}-E^{(2)})\Psi^{(0)} , \tag{B14}$$

etc. Comparing Eqs. (B6) and (B12) we conclude that

$$E^{(0)}=E_e^{(0)} , \tag{B15}$$

and that $\Psi_e^{(0)}$ is a solution of (B12). Since $H_0^{(0)}$ and $\Psi_e^{(0)}$ are independent of U, $\Psi^{(0)}$ has the form

$$\Psi^{(0)}(r,U)=X^{(0)}(U)\Psi_e^{(0)}(r) , \tag{B16}$$

where $X^{(0)}$ will be determined by higher-order equations.

Next, consider the first-order equations (B13). Its solubility condition is

$$\langle\Psi^{(0)}|(H_0^{(1)}-E^{(1)})\Psi^{(0)}\rangle_r = |X^{(0)}(U)|^2\langle\Psi_e^{(0)}|(H_0^{(1)}-E^{(1)})\Psi_e^{(0)}\rangle_r=0 , \tag{B17}$$

where $\langle\ \rangle_r$ denotes integration with respect to r. However, it follows from Eq. (B7)

$$\langle\Psi_e^{(0)}|(H_0^{(1)}-E_e^{(1)})|\Psi_e^{(0)}\rangle_r = -\langle\Psi_e^{(0)}|H_0^{(0)}-E_e^{(0)}|\Psi_e^{(1)}\rangle_r=0 , \tag{B18}$$

with the last equality following from the hermiticity of $H_0^{(0)}$. Equations (B17) and (B18) give the condition

$$E^{(1)}=E_e^{(1)} . \tag{B19}$$

$E^{(1)}$ is a constant (by definition), whereas $E_e^{(1)}$ is linear and homogeneous in U (by construction). Thus Eq. (B19) can only be satisfied if $E_e^{(1)}$ vanishes identically:

$$E_e^{(1)}\equiv\sum_n^{N_n}[\partial E_e(R)/\partial/\mathbf{r}_n]_{R=R_0}\cdot\mathbf{U}_n\equiv 0 , \tag{B20}$$

with $\mathbf{U}_n$ an arbitrary displacement of the nth nucleus, and the sum is taken over all nuclei. We conclude that R_0 must be an equilibrium configuration, i.e.,

$$[\partial E_e(R)/\partial\mathbf{r}_n]_{R=R_0}=0 . \tag{B21}$$

Setting $E^{(1)}=E_e^{(1)}=0$ in Eqs. (B7), (B8), etc., and Eqs. (B13), (B14), etc., allows us to proceed with solving for $\Psi^{(1)}$, $\Psi^{(2)}$, etc. The details become increasingly involved and are irrelevant for our discussion. It suffices to say that solubility conditions for higher-order equations provide equations for $X^{(0)}(U)$ to $X^{(2)}(U)$ (needed for $\Psi^{(1)}$ and $\Psi^{(2)}$), and that $\Psi^{(3)}$ and high-order terms cannot be expressed in separable form. The single most outstanding result of the BO analysis is the condition (B21); without its fulfillment the treatment fails.

APPENDIX C: INVARIANCE OF INTERNAL ANGULAR MOMENTUM

In this appendix I will provide the proof of the invariance of the internal angular momentum under the transformation to coordinates $\mathbf{r}_i$ according to (A5).

First I will prove that the total angular momentum operator defined as

$$\mathbf{J}_M=\bar{i}\hbar\sum_{j=1}^{N}\mathbf{q}_j\times\nabla_j,\quad \bar{i}=-\sqrt{-1} \tag{C1}$$

with ∇_i the gradient operator associated with LF coordinates $\mathbf{q}_i$, is invariant to any nonsingular coordinate transformation defined by

$$\mathbf{q}_i'=\sum_{j=1}^{N}D_{ij}\mathbf{q}_j . \tag{C2}$$

The matrix must be nonsingular, i.e., $|D|\neq 0$. We then have the inverse transformation

$$\mathbf{q}_i=\sum_{j=1}^{N}D_{ij}^{-1}\mathbf{q}_j' , \tag{C3}$$

with obvious notation. ∇_i can be written as

$$\nabla_i=\sum_{j=1}^{N}\frac{\partial\mathbf{q}_j'}{\partial\mathbf{q}_i}\nabla_j'=\sum_{j=1}^{N}D_{ji}\nabla_j' . \tag{C4}$$

Therefore, $\mathbf{J}$ transforms as follows:

$$\mathbf{J}_M=\bar{i}\hbar\sum_{i=1}^{N}\sum_{j,k=1}^{N}D_{ij}^{-1}D_{kj}\mathbf{q}_j'\times\nabla_k'=\bar{i}\hbar\sum_{j=1}^{N}\mathbf{q}_j'\times\nabla_j' . \tag{C5}$$

The last equality follows directly upon interchange of the (j,k) and i summations, and use of the definition of the inverse matrix. We find that $\mathbf{J}$ is invariant if D^{-1} exists.

Secondly, I will prove that the transformation to coordinates $\{\mathbf{R},\mathbf{r},\ldots,\mathbf{r}_{N-1}\}$ as defined by Eqs. (A1) and (A5) is a nonsingular transformation. Inspection of these equations shows that the transformation matrix has the structure

$$D=\begin{vmatrix}\alpha_1 & \alpha_2 & \alpha_3 & \cdots & \alpha_{N-1} & \alpha_N\\ 1 & 0 & 0 & \cdots & 0 & -1\\ 0 & 1 & 0 & \cdots & 0 & -1\\ 0 & \cdots & \cdots & \cdots & 1 & -1\end{vmatrix} , \tag{C6}$$

with $\alpha_i=m_i/M$. Expansion of $|D|$ with respect to elements of the first column immediately shows an inductive route to proving

$$|D|=(-1)^{N-1}\sum_{i=1}^{N}\alpha_i . \tag{C7}$$

Since α_i are all positive definite, we conclude that D is nonsingular.

Because of the proven invariance expressed by (C5), with $\mathbf{q}_N'=\mathbf{R}$, the obvious separation of $\mathbf{J}_M$ in c.m. and internal components occurs:

$$\mathbf{J}_M=\mathbf{J}_{\text{c.m.}}+\mathbf{J} , \tag{C8}$$

with

$$\mathbf{J}_{\mathrm{c.m.}}=-i\hbar\mathbf{R}\times\nabla_R \ , \qquad (\mathrm{C9})$$

$$\mathbf{J}=-i\hbar\sum_{i=1}^{N-1}\mathbf{r}_i\times\nabla_{r_i} \ . \qquad (\mathrm{C10})$$

Since the internal Hamiltonian is invariant to infinitesimal rotations about any axis in the noninertial frame of reference (due to the scalar character of K_i and K_{ij}) it follows immediately that

$$[H,\mathbf{J}]=0 \ , \qquad (\mathrm{C11})$$

i.e., the internal angular momentum is a conserved quantity. Furthermore, due to the homogeneity and isotropy of space, inversion i_N through the position $\mathbf{q}_N$ of the origin of the noninertial frame should commute with H:

$$[H,i_N]=0 \ , \qquad (\mathrm{C12})$$

Eqs. (C11) and (C12) show that eigenfunctions Ψ of H can be characterized by $J_{\pm}$, where $J=S,P,D,\ldots$, as usual, and the subscript refers to (anti) symmetry to inversion i_N. Other quantum numbers will arise from permutations among sets of identical particles (electrons, protons, carbons, etc.) that make up the molecule and time-reversal symmetry. The existence of all these quantum numbers strongly supports the use of shells centered at $\mathbf{q}_N$ in my molecular shell model.

---

[*] Permanent address: Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville, FL 32611.

[1] M. Born and R. Oppenheimer, Ann. Phys. (Paris) **84**, 457 (1927); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1955), pp. 166–173.

[2] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, *Molecular Potential Energy Functions* (Wiley, New York, 1984), p. 29–33.

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1955), Appendix VIII.

[4] R. G. Woolley, Adv. Phys. **25**, 27 (1976).

[5] P. Claverie, in *Symmetries and Properties of Non-Rigid Molecules: A Comprehensive Survey,* edited by J. Maruani and J. Serre (Elsevier, New York, 1983), p. 13 and references cited therein; there are several relevant articles in Israel J. Chem. **19**, 3 (1980).

[6] H. Essén, Int. J. Quantum Chem. **12**, 721 (1977).

[7] T. Kato, *Perturbation Theory of Linear Operators* (Springer, New York, 1976), pp. 17, 149.

[8] V. Z. Kresin and W. A. Lester, Jr., in *Mathematical Analysis of Physical Systems,* edited by R. E. Mickens (Van Nostrand, New York, 1985), p. 247.

[9] P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, New York, 1979); G. S. Ezra, Lect. Notes Chem. **28**, 1 (1982).

[10] *Potential Energy Surfaces and Dynamics Calculations,* edited by D. G. Truhlar (Plenum, New York, 1981); *Molecular Collision Dynamics,* Vol. 33 of *Topics in Current Physics,* edited by J. M. Bowman (Springer, New York, 1983); see also M. Baer, in *Theory of Chemical Reactions,* edited by M. Baer (CRC Press, 1985), p. 219.

[11] E. Teller, J. Phys. Chem. **41**, 109 (1937).

[12] H. C. Longuet Higgins, Proc. R. Soc. Ser. A **344**, 147 (1975).

[13] L. Wolniewicz, J. Chem. Phys. **78**, 6173 (1983); W. Kolos, K. Szalewicz, and H. J. Monkhorst, *ibid.* **84**, 3278 (1986); K. Dressler, L. Wolniewicz, and P. Quadrelli, Int. J. Quantum Chem. **29**, 185 (1986); P. Senn, P. Quadrelli, K. Dressler, and G. Herzberg (unpublished). See also the abundant references in these articles.

[14] F. Coester, Nucl. Phys. **7**, 421 (1958).

[15] K. A. Brueckner, Phys. Rev. **100**, 36 (1955).

[16] J. Goldstone, Proc. R. Soc. London, Ser. A **239**, 267 (1957).

[17] J. Hubbard, Proc. R. Soc. London, Ser. A **240**, 539 (1957).

[18] For largely historical reasons peculiar to quantum chemical applications (see Ref. 24), the cluster operators are here denoted by T_k rather than S_k as in Coester's original and subsequent nuclear physics work. No dislike for Coester's notation is implied.

[19] H. Kümmel, K. H. Lührmann, and J. G. Zabolitzky, Phys. Rep. **C36**, 1 (1978).

[20] I. Lindgren and J. Morrison, *Atomic Many Body Theory* (Springer, New York, 1982).

[21] B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984); see also the many references to earlier less accurate calculations.

[22] R. F. Bishop and K. H. Lührmann, Phys. Rev. B **17**, 3757 (1978); **26**, 5523 (1982).

[23] K. H. Lührmann, Ann. Phys. (N.Y.) **103**, 253 (1977); P. Hoodbhoy and J. W. Negele, Phys. Rev. C **18**, 2380 (1978).

[24] J. Cizek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969).

[25] R. J. Bartlett, Ann. Rev. Phys. Chem. **32**, 359 (1981).

[26] R. F. Bishop and H. Kümmel, Phys. Today **40**(3), 52 (1987).

[27] J. W. Negele, Rev. Mod. Phys. **54**, 913 (1982); see also Phys. Today **38**(4), 24 (1985).

[28] A. Fröman and J. L. Kinsey, Phys. Rev. **123**, 2077 (1961).

[29] M. D. Girardeau, Phys. Rev. A **28**, 3635 (1983).

[30] L. Z. Stolarczyk and H. J. Monkhorst, Int. J. Quantum Chem. **S18**, 267 (1984).

[31] H. J. Monkhorst, Int. J. Quantum Chem. **S11**, 421 (1977); E. Dalgaard and H. J. Monkhorst, Phys. Rev. A **28**, 1217 (1983).

[32] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. **S18**, 255 (1984); J. Chem. Phys. **84**, 2726 (1986); R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties,* edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986), pp. 35–61.

[33] Notice the noncommutation of $\dot{T}$ and T.

[34] H. C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963).

[35] I. L. Thomas, Phys. Rev. **185**, 90 (1969); Phys. Rev. A **2**, 1200 1675 (1970); **3**, 565 (1971); **4**, 2120 (1971); **5**, 1104 (1972).

[36] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **81**, 2723 (1984).

[37] H. J. Monkhorst, in *Comparison of Ab Initio Quantum Chemistry with Experiment: State of the Art,* edited by R. J. Bartlett (Reidel, Dordrecht, 1985), p. 463.

[38] K. Wenzel, J. G. Zabolitzky, B. Jeziorski, K. Szalewicz, and H. J. Monkhorst, J. Chem. Phys. **85**, 3964 (1986).

[39] S. Alexander and H. J. Monkhorst, Int. J. Quantum Chem.

(to be published).

[40] S. K. Mukhopadhyay, D. Sinha, M. D. Prasad, and D. Mukherjee, Chem. Phys. Lett. **117**, 437 (1985); R. J. Bartlett and M. Rittby (unpublished). $T_2^{(r)}$ must be included to provide a description of excited states consistent with that of the ground state.

[41] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, New York, 1984).

[42] E. B. Wilson, Int. J. Quantum Chem. **S13**, 5 (1979); see also Woolley (Ref. 45) for a response.

[43] H. Kümmel and K. H. Lührmann, Nucl. Phys. **A191**, 525 (1972).

[44] J. da Providencia, Nucl. Phys. **61**, 87 (1965); J. Cizek, Adv. Chem. Phys. **14**, 35 (1969).

[45] H. H. Grelland, Int. J. Theor. Phys. **24**, 179 (1985); R. G. Woolley, Chem. Phys. Lett. **125**, 200 (1986).

[46] A. Fröman, J. Chem. Phys. **36**, 1490 (1962); R. T. Pack and J. O. Hirschfelder, *ibid.* **52**, 521 (1970).