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Impact of the Born–Oppenheimer Approximation on Aerothermodynamics

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The Born–Oppenheimer approximation is a mathematical method in quantum mechanics describing quantification and allocation of the energy associated with molecular internal structure. The macroscopic extrapolation to gas mixtures of the microscopic characterization ensuing from the Born–Oppenheimer approximation consists of the typical energy separation in electronic, vibrational, and rotational contributions. This study addresses the legitimacy and pursues the quest of the physical foundations of this macroscopic extrapolation. The importance of thermodynamics in fluid dynamics is synthetically reviewed and its link which leads, through the linear irreversible theory, to the expression of the heat flux is described. The concept of separation of a system into independent subsystems is discussed from the point of view of quantum statistical thermodynamics and applied to a gas to bring forth the identification of the molecular degrees of freedom. The investigation shows unequivocably that the sought foundations do not exist and that the macroscopic extrapolation of the electronic–vibrational–rotational separation is illegitimate because it infringes the basic quantum statistical recipe to obtain macroscopic observables of a physical system. A more physically consistent identification of molecular degrees of freedom is proposed. The impact on aerothermodynamics practices is discussed. Recommendations and guidelines to deal with this critical situation are provided.

Nomenclature

C = normalization coefficient
E = energy constant in Schrödinger equation
$\hat{E}$, $\bar{E}$ = energy constants in Schrödinger equations of noninteracting [ˆ], [¯] molecules
$\hat{E}_i$, $\bar{E}_j$ = quantum-state energies relative to noninteracting [ˆ], [¯] molecules
E_{s} = energy of sth quantum state of system
E_μ = energy constant in Schrödinger equation of μth molecule
E^t_μ, E^i_μ = energy constant in translational, internal Schrödinger equation of μth molecule
H = classical-mechanics Hamiltonian function (system)
$\hat{H}$, $\bar{H}$ = classical-mechanics Hamiltonian functions (subsystem)
h = Planck constant, $6.6260693 \times 10^{-34}\ \mathrm{J \cdot s}$
$h_{\epsilon\delta}$ = enthalpy (per unit component mass) of δth MDoF of ϵth component
$\mathbf{J}_{m_\epsilon}$ = component-mass diffusive flux
$\mathbf{J}_U$ = internal-energy diffusive flux
ℓ_ϵ = number of MDoFs of ϵth component
Ma = Mach number
M_μ = mass of μth molecule
$M_{\mu a}$ = mass of ath material particle (nucleus or electron) in μth molecule
m = mass
$\hat{m}_a$, $\bar{m}_b$ = masses of material particles in [ˆ], [¯] molecules
m_ϵ = mass of ϵth component
N = number of molecules in one-component gas
n = number of components
$\hat{n}$, $\bar{n}$ = number of material particles in [ˆ], [¯] molecules
n_μ = number of nuclei and electrons in μth molecule
$\hat{P}_i$, $\bar{P}_j$ = quantum-state probabilities relative to noninteracting [ˆ], [¯] molecules
P_n = electronic-state probability (Born–Oppenheimer approximation)
P_{nsr} = internal-state probability (Born–Oppenheimer approximation)
P^{ns}_r = rotational-state probability (Born–Oppenheimer approximation)
P^n_s = vibrational-state probability (Born–Oppenheimer approximation)
P_{s} = probability of sth quantum state of system
p = generalized momenta
$\hat{p}$, $\bar{p}$ = generalized momenta (subsystem)
q = generalized coordinates
$\hat{q}$, $\bar{q}$ = generalized coordinates (subsystem)
$\mathbf{R}^{\mathrm{cm}}_\mu$ = position vector of center of mass of μth molecule
$\mathbf{R}_{\mu a}$ = position vector of ath material particle (nucleus or electron) in μth molecule
$\hat{\mathbf{r}}$, $\bar{\mathbf{r}}$ = coordinate sets relative to material particles in [ˆ], [¯] molecules
$\mathbf{r}_{\mu a}$ = internal position vector of ath material particle in μth molecule
S = entropy
S_ϵ = entropy of ϵth component
$S_{\epsilon\delta}$ = entropy of δth MDoF of ϵth component
T = temperature
$T_{\epsilon\delta}$ = temperature of δth MDoF of ϵth component
U = internal energy
U_ϵ = internal energy of ϵth component
$U_{\epsilon\delta}$ = internal energy of δth MDoF of ϵth component
V = volume, potential energy
$\hat{V}$, $\bar{V}$ = potential energies of noninteracting [ˆ], [¯] molecules
$\mathcal{V}_\mu$ = potential energy of μth noninteracting molecule
$\lambda'_{\epsilon\delta}$ = (primed) thermal conductivity of δth MDoF of ϵth component
ψ = wave function
$\hat{\psi}$, $\bar{\psi}$ = wave functions of noninteracting [ˆ], [¯] molecules
ψ_μ = wave function of μth molecule
ψ^t_μ, ψ^i_μ = translational, internal wave function of μth molecule

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Subscripts

a = material particles in μth molecule
a, b = material particles in [$\hat{\ }$], [$\bar{\ }$] molecules
i, j = subsystem quantum states
s = system quantum states
δ = molecular degrees of freedom
ϵ = components
μ = molecules

I. Introductory Reflections

ONE of the finest, although perhaps the most excruciating, problems that we aerothermodynamicists have to deal with is the detailed prediction of the hypersonic-flow field around a spacecraft (re)entering a planetary atmosphere, particularly in correspondence to the flight conditions at which the thermal-load distribution attains maximum intensity. Our duty comprises accurate estimate and reliable provision of flowfield information to heat-shield designers. We are well aware that the physical phenomenology of hypersonic flows presupposes the interplay of a variety of fundamental disciplines, such as thermodynamics, chemical and thermal kinetics, diffusion theory, radiation, gas-surface interactions, etc., which develops within the common fluid-dynamics background. We know that this interplay is extremely complex and that we do not master it completely well. A few of us strive to push ahead the understanding of the physical phenomenology; most of us trust the state-of-the-art understanding of it and aim at exploiting the avenues of computational fluid dynamics and wind-tunnel testing, confiding in their pros and compromising with their cons. In practice, the execution of our duty emerges as the outcome of concerted efforts involving exploitation of both avenues to different degrees of depth.

Notwithstanding our strenuous efforts, there is a feeling of dissatisfaction among (at least some of) us because, let us face it, the error margins of our thermal-load predictions are too large; and that adds on top of other uncertainties, such as those related to atmosphere composition, for example. Ultimately, still today the design of thermal-protection shields relies mainly on extensive, and expensive, wind-tunnel testing, last-minute fixes, and safety factors based on the designer's experience. Clearly, this approach constrains the sizing of the shield to compromise with the burden of ample safety margins that penalize payload mass; it is also not viable for missions with extreme (re)entry speeds because the payload mass may turn out to be negative.

We may be tempted to attribute the reason of our dissatisfaction to limits and drawbacks of computational fluid dynamics and wind-tunnel testing and to believe that, after all, achievement of successful progress is just a matter of refining the tools. There is perhaps a part of truth in this viewpoint. Yet, we should not rule out the conjecture that the root of dissatisfaction resides mainly in our insufficient understanding of the physical phenomenology we are dealing with. Two clear philosophies emerge. Some of us maintain that there are many conceptual weaknesses in the puzzle and that it is difficult to assess their relative importance. Additionally, it would take an unaffordable amount of time to organize and carry out a plan of systematic theoretical investigations to resolve them. It is better to use the resources to refine the tools and deal with planetary-(re)entry missions on a case-by-case approach. Others cannot help but noticing that such a conservative philosophy, based on ad hoc intervention, did not bring the efficiency of our duty performance much farther ahead than that which characterized the aerothermodynamicists' capabilities used at the times of the Apollo program. They disagree with the procrastinating attitude ruling in the conservative camp and feel that it is time to set the house in order. There is no evident scientific way to prove or disprove the validity of either of these philosophies. It is just a matter of personal professional taste. The writer belongs to the latter camp and the discipline chosen for scrutiny here is thermodynamics.

II. Importance of Thermodynamics in Fluid Dynamics

We quickly learn in our student years the importance of thermodynamics when dealing with compressible flows. Luckily, life is easy in classical aerodynamics and gas dynamics because we find out from experience that the thermodynamic behavior of a simple homogeneous gas can be characterized in a complete manner, within an axiomatic perspective [1–9], by the fundamental relation that expresses the entropy of the gas

$$S = S(U, V, m) \tag{1}$$

as a function of its internal energy, volume, and mass. [Equation (1) constitutes the basis of the entropic representation. Alternative, and equivalent, representations are possible.] In particular, we do very well with the perfect- or even ideal-gas assumption. The function (1), when referred to unit mass and analytically explicited, provides the necessary thermodynamic information required by the flowfield equations that govern the dynamics of a gas up to moderately supersonic speeds, say $Ma < 3$ as a rule of thumb. The description of the gas thermodynamic behavior based on Eq. (1) scores such a success in applications pertinent to classical aerodynamics and gas dynamics that it hardly offers stimulus to probe in depth the question of how much energy goes in molecule translation and how the remainder is distributed over the molecular internal structure. What really matters for all practical engineering purposes is the knowledge of the total amount of internal energy; molecular-structure considerations raise marginal interest only with concern to specific-heat dependence on temperature and to understand the transition between ideal- and perfect-gas models. Moreover, the same description fits well also the phenomenology involving constant-composition gas mixtures. Therefore, we understand why such a description totally pervades the aerodynamics pertinent to general-aeronautics applications.

The phenomenological picture drifts slightly toward complexity when energy densities in the flowfield increase and, in turn, molecular collisions become more energetic. Chemical reactions appear on the scene and produce nonnegligible variations of the gas composition that need to be accounted for. The thermodynamic system of interest becomes a chemically reacting gas mixture. Following Gibbs [1–4], the natural extension of the fundamental relation (1) is achieved by including the masses of the chemical constituents, or components, in the functional dependence. With the additional complement of entropy additivity, Eq. (1) is replaced with

$$S = \sum_{\epsilon=1}^{n} S_{\epsilon}(U_{\epsilon}, V, m_{\epsilon}) \tag{2}$$

but the assumption of thermal equilibrium

$$\frac{1}{T} = \left(\frac{\partial S_{\epsilon}}{\partial U_{\epsilon}}\right)_{V, m_{\epsilon}} \qquad \epsilon = 1, \ldots, n \tag{3}$$

is still retained. Thermodynamic models based on the fundamental relation (2) serve well applications in combustion and are preliminarily stretched to describe moderately hypersonic flows. Energywise, we still do not look at molecular-structure details.

Of course, the thermal-equilibrium assumption [Eq. (3)] is doomed to become untenable when sufficiently high-energy densities occur in the flowfield, that is, when we step into the realm of aerothermodynamics. Under that circumstance, the internal energies distributed over the molecular degrees of freedom (MDoFs) of each chemical constituent of the gas mixture must be looked at individually and the next step of sophistication consists in characterizing the disequilibrium through the existence of multiple temperatures [7,10,11]. Following Napolitano [7], we can introduce fundamental relations for each MDoF of each component [$S_{\epsilon\delta}(U_{\epsilon\delta}, V, m_{\epsilon})$] and, again by taking advantage of entropy additivity, extend the function (2) as follows:

$$S = \sum_{\epsilon=1}^{n} \sum_{\delta=1}^{\ell_\epsilon} S_{\epsilon\delta}(U_{\epsilon\delta}, V, m_\epsilon) \qquad (4)$$

Temperatures associated with the MDoFs are simply obtained through partial differentiation

$$\frac{1}{T_{\epsilon\delta}} = \left(\frac{\partial S_{\epsilon\delta}}{\partial U_{\epsilon\delta}}\right)_{V,m_\epsilon} \qquad \delta = 1, \ldots, \ell_\epsilon; \qquad \epsilon = 1, \ldots, n \qquad (5)$$

The fundamental relation (4) provides a workable thermodynamic scheme, certainly legitimate within an axiomatic–thermodynamics context, for gas mixtures in chemical and thermal nonequilibrium. Let us consider an important and far-reaching consequence of Eq. (4). Linear irreversible thermodynamics, when fed with Eq. (4), leads to a corresponding form

$$\mathbf{J}_U = -\sum_{\epsilon=1}^{n} \sum_{\delta=1}^{\ell_\epsilon} \lambda'_{\epsilon\delta} \nabla T_{\epsilon\delta} + \sum_{\epsilon=1}^{n} \sum_{\delta=1}^{\ell_\epsilon} h_{\epsilon\delta} \mathbf{J}_{m_\epsilon} + \cdots \qquad (6)$$

for the internal-energy diffusive flux, an important physical variable whose accurate prediction is relevant to the design of thermal-protection shields. The first term on the right-hand side of Eq. (6) defines the heat flux because it represents the internal-energy diffusion provoked by temperature gradients, namely, the energy-transport mechanism referred to as thermal conduction; it is the obvious generalization of the Fourier law for a multitemperature gas mixture. The thermal conductivites (The prime is meaningful in gas kinetic theory [12].) are expected to be provided by the Chapman–Enskog method of the kinetic theory of gases appropriately reformulated for multitemperature circumstances. The second term represents internal-energy diffusion associated with component-mass diffusion; for a given component, each MDoF participates with its enthalpy evaluated at its own temperature. The "···" term represents effects left unspecified because we are not going to touch upon them in this context. (That does not imply in any way that the unspecified effects are not important. Radiation, for example, is one and constitutes by itself a kind of hic-sunt-leones conceptual arena. But, alright, one problem at a time.)

Equations (4–6) are general but formal and, sooner or later, we have to commit to an identification of the MDoFs if we want our thermodynamic scheme to become operative. The canonical picture solidly stored in our minds is the following. We assign two MDoFs ($\ell_\epsilon = 2$) to monatomic components: translational ($\delta = 1$) and electronic ($\delta = 2$). We assign four MDoFs ($\ell_\epsilon = 4$) to diatomic components: translational ($\delta = 1$), electronic ($\delta = 2$), vibrational ($\delta = 3$), and rotational ($\delta = 4$); for polyatomic components, we consider several vibrational modes and ℓ_ϵ increases accordingly. Free electrons have only the translational DoF ($\ell_\epsilon = 1, \delta = 1$). The imposition of this canonical scheme of MDoF identification (CS-MDoF) on Eqs. (4–6) allows us to talk of and operate with translational, electronic, vibrational, rotational entropies, energies, enthalpies, and so on. We calculate the latter thermodynamic properties from partition functions conveniently factored to allow appearance of distinct temperatures. Single-temperature partition functions originate from the Boltzmann statistics [13] and have a solid basis in statistical thermodynamics. (The Denbighs [14] provided an interesting and rather exhaustive survey of statistical approaches, nicely characterized by a rich bibliography, although with some imprecisions regarding Boltzmann's entropy additivity whose rectification can be found in the very synthetic collection of lectures on statistical thermodynamics given by Schrödinger [15].) Yet, Boltzmann began his analysis with the consideration of a point-particle gas and, after having laid down the basic statistical concepts, he went straight on to deal with mixtures of polyatomic gases [The relevant equations in [13] are Eq. (3) on p. 385 and Eq. (49) on p. 414.] without considering the possibility to allow the MDoFs to play a role in his statistics. Boltzmann's lack of consideration for MDoFs has propagated in time and even in modern statistical treatments the MDoFs surface on the scene at the end of the analysis, only after that the partition-function construct has been fully developed. As a result, the generalization of single-temperature partition functions to embrace multitemperature circumstances is done on an ad hoc basis. (It is easy to sympathize with the following admonition emitted by Keck [16]: "…many workers have used the multiple temperature approximation in applied calculations without inquiring into the conditions for its validity.") Indeed, there are examples [17] that pave the way for the introduction of distinct temperatures by factoring the partition functions with complete disregard of the couplings among electronic, vibrational, and rotational contributions. There are also examples that do not disregard the couplings, as the multitemperature nonequilibrium thermodynamical model proposed by Jaffe [18]. He, nevertheless, proceeded [see the paragraph just after Eq. (13) in [18]] to let the single-temperature exponential term of the internal partition function explode into three similar exponentials to accommodate the presumed existence of electronic, vibrational, and rotational temperatures without reflecting if such a maneuver is statistical thermodynamically sound and justified. As a matter of fact, Jaffe himself pointed out an alarm bell residing in his expression [see Eq. (13) in [18]] of the energy eigenvalue of the internal Schrödinger equation of a molecule: "The question still remains as to how E_{inter} should be partitioned between E'_{vib} and E'_{rot}. Unfortunately there is no unique answer owing to the fact that E_{inter} arises from the unseparability of vibration and rotation." In other words, where do we put the interaction energy (E_{inter}), which, by the way, depends inseparably on all three quantum numbers (electronic, vibrational, rotational): with vibration (E'_{vib}) or with rotation (E'_{rot})? Jaffe concluded that there is no way to resolve the dichotomy. On the other hand, it is clear that, *according to the arbitrary choice we happen to make,* we will obtain different couples of vibrational/rotational temperatures and different contributions to the heat flux on the right-hand side of Eq. (6). We have reached a startling conclusion: the internal-energy diffusive flux [Eq. (6)] depends on our choice of how to apportion the interaction energy between vibration and rotation.

Obviously, this cannot be. And there are admonitions [19,20] in the literature that have already raised concern. So, let us ask ourselves an important question: what is the physical, rational basis upon which we entrust introduction and justification of our CS-MDoF for di/polyatomic molecules? Some may be taken aback by such a question. After all, molecular spectra became available well before the advent of quantum mechanics and it was only natural that scientists of that time, given the classical-mechanics background in which they were used to operate, tried to interpret the spectra in terms of the mental picture that molecules vibrate and rotate. [Sutcliffe provided interesting details about this aspect in Sec. I (Introduction) and Sec. II (History) of [21], together with an adequate list of bibliographic references.] We learn from our student years that a polyatomic molecule can translate, rotate, own one or more vibrational modes, and, to complete the picture, has a certain number of electrons that move incessantly around the nuclei. (See, for example, Fig. 11.1 on p. 416 of Anderson's textbook [17].) True, we are well aware and concede that this is a classical-mechanics intuitive description but the famous article by Born and Oppenheimer [22] on the quantum theory of molecules appeared in 1927 in the prestigious Annalen der Physik and, thanks to it, we feel safely shielded against the anxiety that the intuitive-description objection may introduce by the typical valve of relief reverberating in the aerothermodynamics community: there is the Born–Oppenheimer approximation. Yes, there is. Yet, we cannot deny the suspicion that maybe there is some conceptual weakness in this electronic–vibration–rotation picture or, perhaps, just in its extrapolation from the microscopic to the macroscopic level because, just one paragraph ago, we have stumbled upon the hurdle of the heat-flux arbitrariness.

Perhaps, to brush off the dubiety raised by that suspicion, it is convenient to listen to Einstein's wise advice [23]:

> Concepts which have proven useful for the orderliness of things easily acquire for us such an authority that we forget their terrestrial origins and accept them as immutable facts. They become, then, labeled as "conceptual necessities," "a priori data," and so on. The way of scientific progress is often made unpracticable for a long

> time by such mistakes. It is, therefore, not an idle game at all if we become trained to analyze concepts for a long while familiar and to point out which circumstances their justification and usefulness depend on, how they have separately grown from the facts of experience. In this way, their dominant authority will also be broken. They are put aside if they cannot properly legitimate themselves, corrected if their relationship to given facts also becomes insufficient, subseded by others if a new system lets itself establish that we prefer for some reasons.

and to make the effort to invest a few moments of meditation to find an answer to the important question we formulated above regarding MDoF identification. Advocates of state-to-state kinetical methods may object that the argumentation risks to be moot because we have experimental evidence that there can be situations in which quantum-state population distributions refuse to align themselves along the Boltzmann's paradigm and, in so doing, they cause the whole conceptual edifice built on Eq. (4) to collapse. The counterobjection is that Eq. (4) is just an entry point of convenience for our subject matter. The considerations elaborated and the conclusions achieved in the following sections settle themselves at a level standing conceptually well above the occurrence of analytical or state-to-state population distributions. Our program is, therefore, set: we will engage in the quest of the rational physical basis on which we can hinge the CS-MDoF described above. Let us be prepared: we cannot rely on classical mechanics for our endeavour but we must walk straight, and with due circumspection, through the domain of quantum mechanics.

III. System, Subsystems, and the Concept of Separation

What does it mean to separate a physical system in subsystems? There can be different answers according to the perspectives from which we analyze a particular problem involving our physical system. In classical mechanics, for example, we can characterize every detail of the dynamic evolution of a mechanical system when the knowledge of its Hamiltonian $H(q, p)$ is explicitly available to us. It may happen that we find it useful to identify subsets of the generalized coordinates and momenta, say $(\hat{q}, \hat{p})$ and $(\bar{q}, \bar{p})$, maybe because we operate according to a given criterium of selective convenience or maybe because, in so doing, our intuition perceives hints from the nature of the problem we are trying to solve that we may achieve some simplification, and so on. Conceptually, therefore, the idea settles in our mind that we have seemingly separated the mechanical system in two subsystems identified by the physical parts that distinctively correspond to the chosen subsets of coordinates and momenta. Now, if the Hamiltonian emerges mathematically unaltered $[H(\hat{q}, \bar{q}, \hat{p}, \bar{p})]$ from our subsystem identification then our separation is nothing else than a *merely formal and arbitrary act* dictated by anthropomorphic necessity, namely, our particular choice to categorize coordinates and momenta, injected into the global physical picture for reason of subjective convenience. This formal act of separation may, perhaps, be useful for us but there is no more physical content in doing with it than doing without it. For example, regardless of our separation, the system energy does not turn out to be the sum of the subsystem energies, provided that we can somehow even define the latter. If the Hamiltonian also separates $[H(q, p) = \hat{H}(\hat{q}, \hat{p}) + \bar{H}(\bar{q}, \bar{p})]$ then there is deeper physical significance attached to our subsystem identification and system separation.

To see how the appropriate concept of separation unravels within a quantum-mechanics context, let us consider the simple ensemble of two molecules, each comprising, respectively, $\hat{n}$ and $\bar{n}$ material particles (nuclei, electrons, etc.), and let us write their Schrödinger equation in the convenient form

$$-\frac{h^2}{8\pi^2}\sum_{a=1}^{\hat{n}}\frac{1}{\hat{m}_a}\frac{1}{\psi}\nabla_a^2\psi - \frac{h^2}{8\pi^2}\sum_{b=1}^{\bar{n}}\frac{1}{\bar{m}_b}\frac{1}{\psi}\nabla_b^2\psi + V(\hat{\mathbf{r}}, \bar{\mathbf{r}}) = E \tag{7}$$

In Eq. (7), $\hat{\mathbf{r}}$ and $\bar{\mathbf{r}}$ indicate, respectively, the $3\hat{n}$ and $3\bar{n}$ coordinates of the material particles belonging to the molecules; ∇_a^2 and ∇_b^2 are Laplace operators in terms of those coordinates. The potential energy V of the two-molecule system depends generally on all coordinates and so does the wave function ψ. In the event that the two molecules do not interact, the potential energy becomes separable in two independent contributions

$$V(\hat{\mathbf{r}}, \bar{\mathbf{r}}) = \hat{V}(\hat{\mathbf{r}}) + \bar{V}(\bar{\mathbf{r}}) \tag{8}$$

For simplicity, we assume that each of the potential energies $\hat{V}(\hat{\mathbf{r}})$ and $\bar{V}(\bar{\mathbf{r}})$ cannot be further separated. In this situation, we can attempt to find a separated-variable solution

$$\psi(\hat{\mathbf{r}}, \bar{\mathbf{r}}) = \hat{\psi}(\hat{\mathbf{r}}) \cdot \bar{\psi}(\bar{\mathbf{r}}) \tag{9}$$

for the unknown wave function. The substitution of Eqs. (8) and (9) into Eq. (7) yields

$$\left[-\frac{h^2}{8\pi^2}\sum_{a=1}^{\hat{n}}\frac{1}{\hat{m}_a}\frac{1}{\hat{\psi}}\nabla_a^2\hat{\psi} + \hat{V}(\hat{\mathbf{r}})\right] + \left[-\frac{h^2}{8\pi^2}\sum_{b=1}^{\bar{n}}\frac{1}{\bar{m}_b}\frac{1}{\bar{\psi}}\nabla_b^2\bar{\psi} + \bar{V}(\bar{\mathbf{r}})\right] = E \tag{10}$$

Equation (10) reflects the mathematical structure

$$\begin{bmatrix}\text{differential form}\\ \text{involving}\\ \text{only the } \hat{\mathbf{r}} \text{ coordinates}\end{bmatrix} + \begin{bmatrix}\text{differential form}\\ \text{involving}\\ \text{only the } \bar{\mathbf{r}} \text{ coordinates}\end{bmatrix} = E \tag{11}$$

whose fulfillment can be achieved if, and only if, the differential forms are constant [24,25]

$$-\frac{h^2}{8\pi^2}\sum_{a=1}^{\hat{n}}\frac{1}{\hat{m}_a}\frac{1}{\hat{\psi}}\nabla_a^2\hat{\psi} + \hat{V}(\hat{\mathbf{r}}) = \hat{E} \tag{12}$$

$$-\frac{h^2}{8\pi^2}\sum_{b=1}^{\bar{n}}\frac{1}{\bar{m}_b}\frac{1}{\bar{\psi}}\nabla_b^2\bar{\psi} + \bar{V}(\bar{\mathbf{r}}) = \bar{E} \tag{13}$$

Consequently, the energy constant of the original Schrödinger equation becomes additive

$$E = \hat{E} + \bar{E} \tag{14}$$

The physical interpretation of such a mathematical situation is that the original quantum system, the two-molecule ensemble, is separable in or composed of two independent quantum subsystems, the [ˆ] molecule and the [¯] molecule. The subsystems are independent because they do not interact [Eq. (8)]. They possess their own private Schrödinger equations (12) and (13) which do not exchange any physical information between themselves and can, and must, be solved separately. Both subsystems have their private quantum states on which we can operate statistically [10,11] in a separate and independent manner. Thus, the quantum-state energies $\hat{E}_i$ and $\bar{E}_j$ are provided by the solution of the Schrödinger equations (12) and (13) and we can legitimately introduce for each subsystem's quantum states the corresponding probabilities $\hat{P}_i$ and $\bar{P}_j$; these probabilities are subjected to normalization conditions

$$\sum_i \hat{P}_i = 1 \tag{15}$$

$$\sum_j \bar{P}_j = 1 \tag{16}$$

Now, the system quantum states are identified by two quantum numbers

$$s \equiv \{i, j\} \tag{17}$$

and the next obvious question to address is how quantum states, quantum-state probabilities, and quantum-state energies at subsystem level must be combined to obtain their counterparts at system level. For the quantum-state energies, the answer is easily found from Eq. (14); it must be

$$E_s = \hat{E}_i + \bar{E}_j \tag{18}$$

For the subsystem quantum-state probabilities, we can take advantage of Planck's words (p. 27 of [26]) to introduce an important statistical theorem: "… the probability of two independent systems is equal to the product of the probabilities of each one of the composing systems …" although with a little modification to slightly enhance the correctness of his statement: we interpret "equal" as proportional. Thus

$$P_s = C \cdot \hat{P}_i \cdot \bar{P}_j \tag{19}$$

The proportionality coefficient C must be found from the normalization condition

$$\sum_s P_s = 1 \tag{20}$$

The possibility of imposing Eq. (19), an extremely essential element in the context of the present discourse, is rigidly founded on the statistical independence of the subsystems which, in turn, is enforced mathematically by the fact that we have been able to put the original Schrödinger equation (7) in the form of Eq. (10) and to generate the Schrödinger equations (12) and (13). Planck himself felt the need to stress this point as follows (pp. 28–29 of [26]):

> I will add only one final remark, extremely important, really; this remark relates to the link established between the notions of entropy and probability. We have mentioned before the theorem according to which the probability of a system resulting from the union of two systems is the product of the probability of each of the two composing systems; now this theorem can be only applied in the case of two independent systems, such an independence being understood in the sense meant by the probability calculus. If it is not so, the resulting probability will not be equal to the product of the partial probabilities.

We can draw important deductions of general validity from the analysis of the simple two-molecule system considered thus far. First, the physical legitimacy of the existence of subsystem quantum states, quantum-state probabilities, and quantum-state energies is subdued to the possibility to separate the Schrödinger equation of the system [Eq. (7)] in independent parts [Eq. (10)] that identify the independent subsystems which the global system can be thought separated in or composed of and that produce the Schrödinger equations (12) and (13) governing those subsystems. Hereinafter, let us refer to such an occurrence as the statistically demanded Schrödinger-equation separability condition, SESC in short. Secondly, SESC implies the statistical independence of the identified subsystems and, according to Planck's "extremely important final remark," presupposes the applicability of the probability-product theorem [Eq. (19)]. Finally, the potential energy plays the key role as primary agent in allowing and driving [Eq. (8)] the SESC. The essentiality of these considerations is central to the present discourse and can never be stressed enough.

IV. Schrödinger-Equation Separability Condition for One-Component Perfect Gas

A. Identification of Translational and Internal Molecular Degrees of Freedom

We have seen in Sec. III, when dealing with the simple two-molecule example, that physical entities which qualify as subsystems (if any) can be identified only by inspection of the global Schrödinger equation of the system. We take up this task now for a one-component gas composed by N molecules ($\mu = 1, \ldots, N$) all having same nature. Its Schrödinger equation embraces all the molecules and reads

$$-\frac{h^2}{8\pi^2}\sum_{\mu=1}^{N}\sum_{a=1}^{n_\mu}\frac{1}{M_{\mu a}}\frac{1}{\psi}\nabla^2_{\mu a}\psi + V(\text{all }\mathbf{R}_{\mu a}) = E \tag{21}$$

In Eq. (21), $\nabla^2_{\mu a}$ is the Laplace operator $(\partial/\partial\mathbf{R}_{\mu a}\cdot\partial/\partial\mathbf{R}_{\mu a})$ in terms of the position vector $\mathbf{R}_{\mu a}$. The presence of the subscript μ in n_μ and $M_{\mu a}$ is merely formal because each molecule includes the same fixed number $(n_1 = n_2 = \cdots = n_N)$ of nuclei and electrons $(a = 1, \ldots, n_\mu)$ and we are free to enumerate nuclei and electrons of the molecules in a correspondingly consistent manner $(M_{1a} = M_{2a} = \cdots = M_{Na})$. We assume the absence of external fields and perfect-gas behavior of the gas. From a microscopic perspective, the latter assumption implies the recognition that interactions among molecules in the gas are negligible and that the potential energy of the gas turns out to be separable as the sum

$$V(\text{all }\mathbf{R}_{\mu a}) = \sum_{\mu=1}^{N}\mathcal{V}_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu}) \tag{22}$$

of the contributions associated with interactions within the molecules. The presence of the subscript μ in $\mathcal{V}_\mu$ is also formal because the same nature of the molecules implies that they feature the same interaction $(\mathcal{V}_1 = \mathcal{V}_2 = \cdots = \mathcal{V}_N)$. The substitution of Eq. (22) into Eq. (21) yields

$$\sum_{\mu=1}^{N}\left[-\frac{h^2}{8\pi^2}\sum_{a=1}^{n_\mu}\frac{1}{M_{\mu a}}\frac{1}{\psi}\nabla^2_{\mu a}\psi + \mathcal{V}_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu})\right] = E \tag{23}$$

Apart from the presence of the wave function, the differential form between brackets in Eq. (23) contains exclusively information relative to the μth molecule. We can, therefore, employ the usual variable-separation technique

$$\psi = \prod_{\mu=1}^{N}\psi_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu}) \tag{24}$$

and reduce Eq. (23) to the form

$$\sum_{\mu=1}^{N}\left[-\frac{h^2}{8\pi^2}\sum_{a=1}^{n_\mu}\frac{1}{M_{\mu a}}\frac{1}{\psi_\mu}\nabla^2_{\mu a}\psi_\mu + \mathcal{V}_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu})\right] = E \tag{25}$$

The mathematical fulfillment of Eq. (25) is possible only if the differential forms in brackets are constants

$$\begin{aligned}&-\frac{h^2}{8\pi^2}\sum_{a=1}^{n_\mu}\frac{1}{M_{\mu a}}\frac{1}{\psi_\mu}\nabla^2_{\mu a}\psi_\mu\\ &\quad + \mathcal{V}_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu}) = E_\mu \qquad \mu = 1, \ldots, N\end{aligned} \tag{26}$$

and the enforcement of energy-constant additivity becomes an obvious consequence

$$\sum_{\mu=1}^{N}E_\mu = E \tag{27}$$

Equations (26) are the private Schrödinger equations of the molecules. They are basically the same equation that repeats N times. If we solve Eq. (26) for one molecule then we have solved it for all molecules.

We can go one step further toward SESC if we consider the physical fact, learned from experience, that the potential energy of a molecule depends only on the relative distances between material-particle pairs belonging to the molecule; in more sophisticated terms, the function $\mathcal{V}_\mu$ is invariant when the molecule is subjected to (virtual) rigid translation and rotation. We calculate the molecule mass

$$M_\mu = \sum_{a=1}^{n_\mu} M_{\mu a} \tag{28}$$

and introduce the position vector of the molecule center of mass

$$\mathbf{R}_\mu^{\mathrm{cm}} = \sum_{a=1}^{n_\mu} \frac{M_{\mu a}}{M_\mu} \mathbf{R}_{\mu a} \tag{29}$$

and the internal position vectors

$$\mathbf{r}_{\mu a} = \mathbf{R}_{\mu a} - \mathbf{R}_{\mu n_\mu} \qquad a = 1, \ldots, n_\mu - 1 \tag{30}$$

reckoned, for example, from the material point $a = n_\mu$ ($\mathbf{r}_{\mu n_\mu} = 0$). With this change of positional coordinates, the functional dependence of the molecule wave function becomes

$$\psi_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu}) \to \psi_\mu\left(\mathbf{R}_\mu^{\mathrm{cm}}, \mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1}\right) \tag{31}$$

and the potential energy turns out to depend only on the internal coordinates

$$\mathcal{V}_\mu(\mathbf{R}_{\mu 1}, \mathbf{R}_{\mu 2}, \ldots, \mathbf{R}_{\mu n_\mu}) \to \mathcal{V}_\mu(\mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1}) \tag{32}$$

The linear combination of the Laplace operators in Eq. (26) can be separated as the sum of two operators

$$\sum_{a=1}^{n_\mu} \frac{1}{M_{\mu a}} \nabla_{\mu a}^2 = \frac{1}{M_\mu} \nabla_\mu^2 + \mathcal{H}_\mu \tag{33}$$

The first operator on the right-hand side of Eq. (33) has the simple definition $\nabla_\mu^2 = \partial/\partial\mathbf{R}_\mu^{\mathrm{cm}} \cdot \partial/\partial\mathbf{R}_\mu^{\mathrm{cm}}$ and acts only on the center-of-mass coordinates; the second operator is slightly more complex

$$\mathcal{H}_\mu = \sum_{a=1}^{n_\mu - 1} \frac{1}{M_{\mu a}} \frac{\partial}{\partial \mathbf{r}_{\mu a}} \cdot \frac{\partial}{\partial \mathbf{r}_{\mu a}} + \frac{1}{M_{\mu n_\mu}} \sum_{a=1}^{n_\mu - 1} \sum_{b=1}^{n_\mu - 1} \frac{\partial}{\partial \mathbf{r}_{\mu a}} \cdot \frac{\partial}{\partial \mathbf{r}_{\mu a}} \tag{34}$$

and acts only on the internal coordinates. We substitute Eqs. (32) and (33) into Eq. (26) to obtain

$$\begin{aligned} &-\frac{h^2}{8\pi^2} \frac{1}{M_\mu} \frac{1}{\psi_\mu} \nabla_\mu^2 \psi_\mu - \frac{h^2}{8\pi^2} \frac{1}{\psi_\mu} \mathcal{H}_\mu \psi_\mu \\ &\quad + \mathcal{V}_\mu(\mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1}) = E_\mu \end{aligned} \tag{35}$$

and then apply the familiar variable-separation technique to Eq. (31)

$$\psi_\mu = \psi_\mu^t\left(\mathbf{R}_\mu^{\mathrm{cm}}\right) \cdot \psi_\mu^i\left(\mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1}\right) \tag{36}$$

to reduce Eq. (35) to the form

$$\begin{aligned} &\left[-\frac{h^2}{8\pi^2} \frac{1}{M_\mu} \frac{1}{\psi_\mu^t} \nabla_\mu^2 \psi_\mu^t\right] \\ &\quad + \left[-\frac{h^2}{8\pi^2} \frac{1}{\psi_\mu^i} \mathcal{H}_\mu \psi_\mu^i + \mathcal{V}_\mu(\mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1})\right] = E_\mu \end{aligned} \tag{37}$$

Upon recognition that the first differential form on its left-hand side contains only center-of-mass coordinates while the second differential form contains only internal coordinates, Eq. (37) generates the translational Schrödinger equation

$$-\frac{h^2}{8\pi^2} \frac{1}{M_\mu} \frac{1}{\psi_\mu^t} \nabla_\mu^2 \psi_\mu^t = E_\mu^t \tag{38}$$

the internal Schrödinger equation

$$-\frac{h^2}{8\pi^2} \frac{1}{\psi_\mu^i} \mathcal{H}_\mu \psi_\mu^i + \mathcal{V}_\mu(\mathbf{r}_{\mu 1}, \mathbf{r}_{\mu 2}, \ldots, \mathbf{r}_{\mu n_\mu - 1}) = E_\mu^i \tag{39}$$

and pushes one level further energy-constant additivity

$$E_\mu^t + E_\mu^i = E_\mu \tag{40}$$

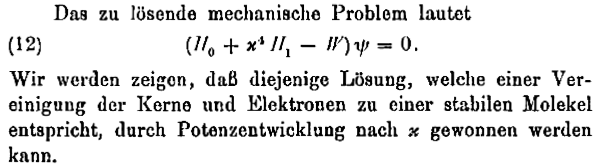
The translational equation (38) does not exhibit any potential energy, does not require any additional separation, and is amenable to analytical solution. The internal equation (39) comprises the potential energy associated with the interactions within the molecule and calls for more attention. At any rate, as a consequence of the separation we have achieved so far, we rest assured that a molecule possesses at least two independent DoFs: translational and internal. But we expect more DoFs and have now reached the right place to deal with a central issue of our investigation: the presumed separability of the internal Schrödinger equation.

B. Internal Schrödinger Equation and Born–Oppenheimer Approximation

The idea of separating the internal Schrödinger equation brings into the discourse the famous quantum theory of molecules formulated by Born and Oppenheimer [22]. (As mentioned in Sec. II, their paper appeared in 1927 but we would really be surprised to find out how sharply accurate the following remark of Robertson is: "The Born–Oppenheimer paper is often cited but seldom read.") The critical question is: can we separate the internal Schrödinger equation (39) any further? With a view to the interaction potentials that nature teaches us to exist, the rigorous and dry answer is no. Nevertheless, the canonical attitude among scientists interested in this matter seems to be that the approximate separation of the internal Schrödinger equation according to the Born–Oppenheimer method is considered to be a nonrigorous but reasonable assumption that works well. But qualification as *reasonable assumption that works well* depends on the applicative context in which one operates. There are subtle and misinterpreted facets overlooked by this canonical attitude—misinterpretations that originate from insufficiently clarified differences about the separation concept that different people may have in their minds when discussing the subject matter. Consequences may lead theory astray. The negative answer given above is based on the idea of separation as demanded by the statistical theory: subdivision of a given entity in independent subentities (Sec. III). In this regard, we should pertinently revisit Planck's words quoted after Eq. (20). The subentity independence is enforced by physically independent Schrödinger equations [for example, from Eq. (25) into Eq. (26), or from Eq. (37) into Eqs. (38) and (39)] obtained by the following guidance from potential energies [Eq. (22)].

Now, what do we actually mean when we say that the internal Schrödinger equation can be approximately separated according to the Born–Oppenheimer method? Guessing an answer on the basis of classical-mechanics intuitive arguments does not help. There is only one meaningful thing to do to provide a satisfactory answer: we have to read the original paper [22]. We, therefore, engage in this task now, although in an obviously synthetic manner; all cross references to the original paper are prefixed by the label "bo."

Essentially, Born and Oppenheimer devised a mathematical method (see Figs. 1 and 2) based on power-series expansions of the Hamiltonian operator ["gesamte Energieoperator"; Eq. bo-(33)], wave function ["Eigenfunktion"; upper Eq. bo-(34)] and energy constant ["Energieparameter"; lower Eq. bo-(34)], appearing in the Schrödinger equation of a polyatomic molecule [Eq. bo-(12), corresponding to Eq. (26)], and discussed the successive-order solutions [Eq. bo-(35a), Eq. bo-(35b), …] of the method. Their expansion parameter $\varkappa$ is the fourth root of the indeed very small ratio electron mass over average nuclear mass. Refinements [27,28] and mathematical sophistications [29,30] (Born and Oppenheimer's idea rested upon ordinary perturbation theory. But nowadays mathematicians would not consider mathematically sound the use of ordinary perturbation theory. This is what led to the work in [29,30]. On the other hand, a completely different approach is possible using coherent-state theory and avoiding perturbation theory altogether [31]. The interesting thing about the coherent-state approach is that it does not depend on expansion about a minimum in

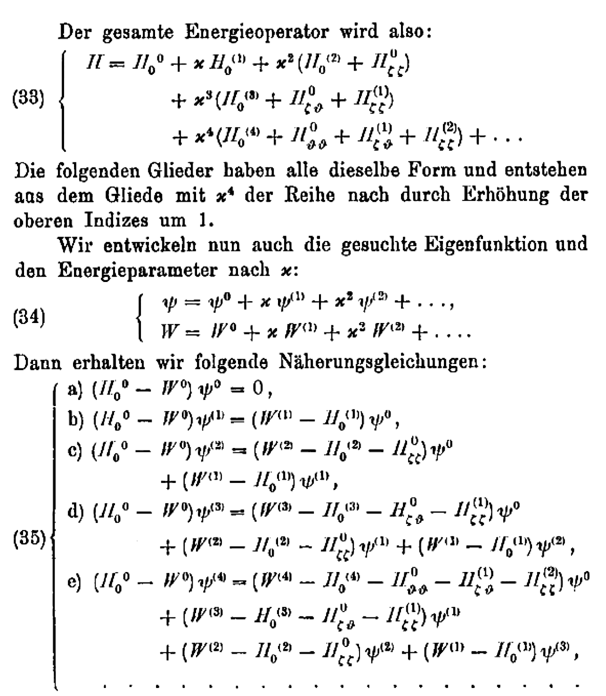


Das zu lösende mechanische Problem lautet

$$(H_0 + \varkappa^4 H_1 - W)\psi = 0. \tag{12}$$

Wir werden zeigen, daß diejenige Lösung, welche einer Vereinigung der Kerne und Elektronen zu einer stabilen Molekel entspricht, durch Potenzentwicklung nach $\varkappa$ gewonnen werden kann.

Fig. 1 Born and Oppenheimer's formulation [22] of the (quantum-) mechanical problem for a polyatomic molecule. Equation bo-(12) corresponds to Eq. (26). The Hamiltonian operator is $H = H_0 + \varkappa^4 H_1$. H_0 represents the sum of the kinetic terms of the electrons and of the molecule potential energy; $\varkappa^4 H_1$ represents the kinetic terms of the nuclei. [Eqs. bo-(4)–bo-(7); not shown here]. The authors say that that solution of Eq. bo-(12) which corresponds to an assembly of nuclei and electrons bound in a stable molecule can be obtained by a power series of the parameter $\varkappa$.



Der gesamte Energieoperator wird also:

$$(33)\quad \left\{ \begin{aligned} H = {} & H_0{}^0 + \varkappa H_0{}^{(1)} + \varkappa^2 (H_0{}^{(2)} + H^0_{\zeta\zeta}) \\ & + \varkappa^3 (H_0{}^{(3)} + H^0_{\zeta\vartheta} + H^{(1)}_{\zeta\zeta}) \\ & + \varkappa^4 (H_0{}^{(4)} + H^0_{\vartheta\vartheta} + H^{(1)}_{\zeta\vartheta} + H^{(2)}_{\zeta\zeta}) + \dots \end{aligned} \right.$$

Die folgenden Glieder haben alle dieselbe Form und entstehen aus dem Gliede mit $\varkappa^4$ der Reihe nach durch Erhöhung der oberen Indizes um 1.

Wir entwickeln nun auch die gesuchte Eigenfunktion und den Energieparameter nach $\varkappa$:

$$(34)\quad \left\{ \begin{aligned} \psi &= \psi^0 + \varkappa \psi^{(1)} + \varkappa^2 \psi^{(2)} + \dots, \\ W &= W^0 + \varkappa W^{(1)} + \varkappa^2 W^{(2)} + \dots. \end{aligned} \right.$$

Dann erhalten wir folgende Näherungsgleichungen:

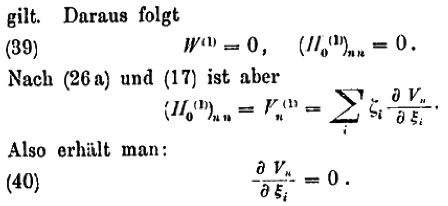
$$(35)\left\{ \begin{aligned} &\text{a)}\ (H_0{}^0 - W^0)\psi^0 = 0, \\ &\text{b)}\ (H_0{}^0 - W^0)\psi^{(1)} = (W^{(1)} - H_0{}^{(1)})\psi^0, \\ &\text{c)}\ (H_0{}^0 - W^0)\psi^{(2)} = (W^{(2)} - H_0{}^{(2)} - H^0_{\zeta\zeta})\psi^0 \\ &\qquad + (W^{(1)} - H_0{}^{(1)})\psi^{(1)}, \\ &\text{d)}\ (H_0{}^0 - W^0)\psi^{(3)} = (W^{(3)} - H_0{}^{(3)} - H^0_{\zeta\vartheta} - H^{(1)}_{\zeta\zeta})\psi^0 \\ &\qquad + (W^{(2)} - H_0{}^{(2)} - H^0_{\zeta\zeta})\psi^{(1)} + (W^{(1)} - H_0{}^{(1)})\psi^{(2)}, \\ &\text{e)}\ (H_0{}^0 - W^0)\psi^{(4)} = (W^{(4)} - H_0{}^{(4)} - H^0_{\vartheta\vartheta} - H^{(1)}_{\zeta\vartheta} - H^{(2)}_{\zeta\zeta})\psi^0 \\ &\qquad + (W^{(3)} - H_0{}^{(3)} - H^0_{\zeta\vartheta} - H^{(1)}_{\zeta\zeta})\psi^{(1)} \\ &\qquad + (W^{(2)} - H_0{}^{(2)} - H^0_{\zeta\zeta})\psi^{(2)} + (W^{(1)} - H_0{}^{(1)})\psi^{(3)}, \\ &\quad \dots\dots\dots\dots\dots\dots\dots\dots \end{aligned} \right.$$

Fig. 2 The successive-order perturbation method.

the potential. However, it is vital for the approach that the considered electronic-energy surface remains isolated. Closely approaching and/or crossing surfaces are still not understood.) of the method have appeared in the literature but the conceptual substance remains unchanged. Comprehensive surveys [32,33] of the method are also available. There is nothing quantum mechanics specific in the mathematics of the Born–Oppenheimer method. The same mathematical technique is exploited to advantage also in other domains. Two examples come easily to mind: the Chapman–Enskog method in the kinetic theory of gases [12] to find the distribution function from the Boltzmann equation through power-series expansion in terms of the Knudsen number; the thin-airfoil method [34] in aerodynamics developed by Munk [35] and Glauert [36] which corresponds to finding, from the Laplace equation, the velocity-vector potential through power-series expansion in terms of the airfoil percentual thickness.

In the first four paragraphs of Sec. bo-3, Born and Oppenheimer declared clearly and unambiguously the limits of their method (p. bo-464):

> An arbitrary configuration of electrons and nuclei does not let itself, of course, to be treated according to a general procedure of approximation. We wish here to consider only those states that correspond to a stable molecule. Therefore, in the beginning we ask the following question:
>
> Is there an ensemble of values of the relative nuclear coordinates ξ_i, of the kind that the eigenfunctions ψ_n of the energy operator [bo-](6), in so far as they depend on the ξ_i, become appreciably different from zero only in a small vicinity of this ensemble of values?
>
> This wave-mechanics problem corresponds evidently to the classical situation in which the nuclei perform only small vibrations around an equilibrium position; then $|\psi_n|^2$ is the probability, therefore, that a determined configuration of given energy possesses.
>
> Thus, we consider as an undisturbed system the motion of the electrons relative to a firstly arbitrary but fixed configuration ξ_i of the nuclei. Then, we develop all the variables in terms of small deviations from the ξ_i that we indicate with $\varkappa\ \zeta_i$; we impose, therefore, that the "vibration extent" tends to zero with $\varkappa$, an assumption which can be justified only through its success.



gilt. Daraus folgt

$$W^{(1)} = 0, \quad (H_0{}^{(1)})_{nn} = 0. \tag{39}$$

Nach (26a) und (17) ist aber

$$(H_0{}^{(1)})_{nn} = V_n{}^{(1)} = \sum_i \zeta_i \frac{\partial V_n}{\partial \xi_i}.$$

Also erhält man:

$$\frac{\partial V_n}{\partial \xi_i} = 0. \tag{40}$$

Fig. 3 The first-order problem and its important condition [Eq. bo-(40)] for the validity of the method: the relative coordinates ξ_i of the nuclei cannot be chosen arbitrarily but must correspond to an extremum of the electronic energy $V_n(\xi_i)$.

It is rather peculiar, if not odd, that this important premise is never mentioned whenever the Born–Oppenheimer method is invoked in support of the presumed separability of the internal Schrödinger equation. Subsequently, the authors set up the successive-order approximation scheme [Eqs. bo-(33)–bo-(35) in Fig. 2] and proceeded to discuss successive-order solutions.

The zero-order solution [Eq. bo-(35a)] pertains "the motion of the electrons for fixed nuclei" and that had already been discussed in Sec. bo-2. With the availability of the zero-order solution one can then proceed to deal with the first-order solution [Eq. bo-(35b)]. The first-order contribution to the energy constant vanishes [Fig. 3; Eq. bo-(39) left] and this occurrence brings forth an important and crucial condition [Eq. bo-(40)] which was emphasized by the authors as (p. bo-467) the following:

> The possibility to proceed with our approximate procedure requires, thus, that the relative coordinates ξ_i of the nuclei cannot be chosen arbitrarily but they must correspond to an extremum of the electronic energy $V_n(\xi)$. The existence of such an extremum is thus the condition for the possibility of existence of the molecule, an assumption that commonly is taken to be self-evident. We will see afterwards that it must necessarily be the case of a minimum.

These salient requirements for applicability have also been rendered with sharp and unambiguous emphasis by Sutcliffe [37] when discussing the Born–Oppenheimer method on pp. 30–31 of [37] [the symbol E in the quote corresponds to E_μ in Eq. (26)]:

> If we solve the fixed nucleus Hamiltonian problem, as usual, for various values of the internal (nuclear) coordinates to determine E as a function of these coordinates and we find that E has a reasonably deep minimum for some values of these coordinates, then we know that we can … develop solutions to the whole molecule problem, as accurately as we choose. The resulting functions are of course good only for the region of configuration space about this minimum but within this region we are on safe ground.
>
> Now of course it is technically possible to solve the fixed nucleus problem, with nuclei fixed at arbitrary positions and so obtain an energy surface (or surfaces) for the complete range of values of the internal coordinates, but … it is problematic in the extreme as to how far it is legitimate to treat such a surface as a "potential" in which to describe nuclear motion, except close to a minimum in that surface. Essentially the situation is this, you can go ahead and solve the problem for the nuclei on the electronic surface you get… and this is now a growing art form. But one cannot be clear about what relation this problem has to the physical situation one wishes to describe, for there are bound to be regions on the surface where

> the whole notion of separation of nuclear and electronic motions becomes nonsense. Thus the fixed nucleus problem for a system does not have an invariant significance over the whole range of internuclear separations, a conclusion which is of course world shatteringly unsurprising.

An impressive statement indeed that leaves no latitude to doubt. Sutcliffe touched on the theme again on p. 35 of [37] and concluded with a warning:

> I do not want to stop people calculating "potential" energy surfaces (so-called) but I wish you always to ask yourselves (if it) is that what they really are.

In aerothermodynamics parlance, Sutcliffe's warning translates into a rather serious and thought-provoking question: what degree of meaningfulness and/or accuracy can we attach to engineering predictions from calculations of high-speed flows involving disequilibrium situations (dissociation, ionization) in which molecules are well away from "an extremum (minimum) of the electronic energy $V_n(\xi)$" if those calculations are based on models in thermodynamics, kinetic theory, chemical kinetics, thermal kinetics, state-to-state kinetics, and radiation that are founded on the molecular-structure picture based on our canonical interpretation of the Born–Oppenheimer approximation?

The second-order solution [Eq. bo-(35c)] describes harmonic oscillations of the nuclei; it also indicates that the extremum originated from Eq. bo-(40) must be a minimum to allow the existence of stable molecules. The third-order contribution to the energy constant vanishes [Eq. bo-(56), not shown here]. The fourth-order solution [Eq. bo-(35e)] consists of a rigid-body motion of the molecule. Translation can be easily disposed of and the authors' discourse concentrated on the more important rotation. Born and Oppenheimer stopped at the fourth-order approximation, emphasized that (p. bo-474)

> The higher(-order) approximations describe the coupling among rotational, vibrational, and electronic motions.

and then summarized the results. Equation bo-(73) provides the fourth-order approximation to the energy constant in the internal Schrödinger equation and constitutes the core ingredient of the Born–Oppenheimer method. The authors wrote (p. bo-474)

> $$W_{nsr} = V_n^0 + \varkappa^2 W_{ns}^{(2)} + \varkappa^4 W_{nsr}^{(4)} + \cdots \qquad (73)$$
>
> where V_n^0 is the minimum value of the electronic energy that characterizes the considered molecule at rest, $W_{ns}^{(2)}$ is the energy of the nuclear vibrations, and $W_{nsr}^{(4)}$ comprises the energy of rotation (to account alongside in addition to the vibrational energy). Thus, in this approximation (up to $\varkappa^4$) the three basic kinds of motion appear "separated"; if one wants to investigate their coupling, higher powers of $\varkappa$ must be considered.

The symbol W on the left-hand side of Eq. bo-(73) corresponds to E_μ^i in Eq. (39) and n, s, r are, respectively, the electronic, vibrational, and rotational quantum numbers that characterize the internal state of the molecule.

With a look at Eq. bo-(73), two questions come to mind. The first question is connected with the limitation imposed by the important condition of the electronic-energy minimum [Eq. bo-(40)] necessary for the applicability of the Born–Oppenheimer method: how good or bad is the numerical approximation provided by Eq. bo-(73), or any other semi-empirical approximation generated thereof by means of coupling/correction factors, when molecules have to endure situations (dissociation, ionization, etc.) far from the electronic-energy minimum? To use a classical-mechanics analogy, the feeling here is that applying Eq. bo-(73) in those situations would be similar to applying the small-oscillation solution of a pendulum motion when the pendulum is swinging between −90 and +90 deg. Well, there is not much that we aerothermodynamicists can do about this question; finding the answer is a task for our colleagues the (computational) quantum chemists. The second question is: can we really say that, with Eq. bo-(73), we have achieved separation? There are two answers: maybe yes from a mathematical point of view just because, following Born and Oppenheimer, we merely choose to leave out the higher-order terms that are responsible for coupling effects; certainly not from a statistical point of view (Sec. III) because quantum electronic-, vibrational-, and rotational-energy manifolds are not generated by independent Schrödinger equations but are linked by a successive-order approximating mathematical procedure in which the *solution at a given order presupposes the knowledge of, and therefore depends on, all the lower-order solutions* [Eq. bo-(35)]. It is the second answer that matters in the context of our discourse. Thus, remembering the last sentence in Planck's quote after Eq. (20), we can safely say that even if we stretch our imagination and succeed in defining electronic, vibrational, and rotational (normalized) quantum-state probabilities (say P_n, P_s^n, P_r^{ns}) somehow (of course, we understand that such definitions are absolutely incompatible with SESC) we will never be able to leap beyond a conceptually insuperable barrier: the product of our imagination-generated electronic-, vibrational-, rotational-state probabilities does not reproduce the internal-state probabilities (say P_{nsr}) which describe the quantum reality of the molecular structure. Mathematically speaking

$$P_{nsr} \neq P_n \cdot P_s^n \cdot P_r^{ns} \qquad (41)$$

So, when we calculate the molecule internal energy in compliance with the necessary quantum-mechanics prescript

$$\underbrace{\sum_{nsr} P_{nsr} W_{nsr}}_{\text{internal}} \neq \underbrace{\sum_{n} P_n \cdot V_n^0}_{\text{electronic}} + \underbrace{\sum_{s} P_s^n \cdot \varkappa^2 W_{ns}^{(2)}}_{\text{vibrational}} + \underbrace{\sum_{r} P_r^{ns} \cdot \varkappa^4 W_{nsr}^{(4)}}_{\text{rotational}} \qquad (42)$$

we must be prepared to accept the solid evidence that, at the macroscopic level, we cannot separate it into electronic, vibrational, and rotational energies. Another very important facet of Eqs. (41) and (42), which we should not make the mistake to miss the recognition of, is that they are true regardless whether we represent the probabilities on the right-hand side of Eq. (41) with analytical distributions or we determine them by state-to-state kinetics.

We should take a moment of reflection when looking at Eqs. (41) and (42) because they teach us a serious lesson (A lesson adequately emphasized by taking advantage, once again, of Sutcliffe's wit —"The only comfortable thing to emerge from the theoretical physicists musings is that they all seem to think that the Born–Oppenheimer approximation is just fine. But precisely why they think so is not clear, at least not in any of the papers that I have read."—because it conveys the exact picture of what the situation is, at macroscopic level, within our community as well. Indeed, we should simply replace "theoretical physicists" with aerothermodynamicists and the statement will suit smoothly.): the conceptual and numerical necessity to go beyond the Born–Oppenheimer approximation for applications in aerothermodynamics is evident. As a matter of fact, such a necessity was perceived and recognized a long time ago, although in other scientific circles. An example is the particularly suitable remark on p. 114 of Teller's memoirs [38] regarding the carbon–dioxide molecule whose properties are of relevance for the aerothermodynamics of Mars- and Venus-atmosphere entry. Teller said:

> I had suggested that he (Rudolf Renner) look at the excited states of the linear (and therefore symmetrical) carbon dioxide molecule, in which the electrons rotate around the axis of the molecule. I suspected that in that case, the Born–Oppenheimer approximation separating the motion of nuclei and electrons did not hold. Renner found that the two kinds of motion were mixed in a more thorough manner, and that, in this case, one cannot describe the motion of the electrons by starting from an approximation in which the nuclei are at rest.

It is nobody's dream to deny or to ignore the tremendous conceptual and computational effort hidden behind the non–Born–Oppenheimer handling of the internal Schrödinger equation (39) but there are attempts [39–44] under way that do not disdain to challenge its presumed unsurmountable mathematical complexity. Outstanding reviews about quantum-chemistry computational methods have been given by Sutcliffe [37] and, more recently and with a view to the future, by Barden and Schaefer [45] and by Jensen and Bunker [46].

Perhaps, the proper way to conclude these considerations regarding the presumed separability of the internal Schrödinger equation is to say a few words of caution: we should not draw from our present discussion the misleading, and certainly wrong, impression that Born and Oppenheimer's mathematical method is incorrect. That is certainly not the case. Their method is perfectly legitimate within its limits of applicability, and these limits were unambiguously stated by those authors. What is wrong is our misuse of their method outside its range of validity and our misinterpretation of Eq. bo-(73) as the required justification to extrapolate the corresponding energy-eigenvalue separation scheme to a macroscopic level.

V. Conclusions

In the light of the argumentations elaborated on in Secs. IV.A and IV.B, and to the dismay of those of us who subscribe to the canonically accepted view of this matter, the following conclusion appears inescapable: the internal Schrödinger equation (39) is nonseparable in the sense required by the statistical theory and the single-molecule Schrödinger equation (37) teaches us that a di/polyatomic molecule has only two DoFs ($\ell_\epsilon = 2$) that statistically qualify as independent quantum subsystems, namely, translational DoF ($\delta = 1$) and internal DoF ($\delta = 2$). Electronic, vibrational, and rotational modes as they arise in the Born–Oppenheimer method do not qualify as such. In this respect, therefore, there is no structural difference between a di/polyatomic molecule and a monoatomic molecule; the only peculiarity of the latter is that internal DoF becomes synonymous with electronic DoF because we have the habit of putting the origin of the internal-coordinate reference frame on its nucleus and, as a consequence of this choice, the internal structure turns out to be exclusively characterized by the electrons. The new scheme of MDoF identification (NS-MDoF) completely removes the arbitrariness of apportioning the interaction energy between vibration and rotation (Sec. II) that afflicts coupling-preserving ad hoc multitemperature schemes [18].

The conclusion we have just drawn puts us in the position to close the discourse we opened with the important question motivating our investigation (paragraph after Jaffe's quote in Sec. II). Indeed we can now definitely and unhesitatingly answer: there is no physical, rational basis which supports our CS-MDoF for di/polyatomic molecules. Those who were taken aback by the question may be perhaps stunned by the answer. Some seek help by turning to spectroscopy. The standard claim would be that there is a huge body of experimental spectroscopic evidence in defense of the CS-MDoF; how can we possibly cast doubts on its physical reality? Well, we have to use prudence and to reflect carefully here. Within an aerothermodynamics perspective, spectroscopic data have always been, and still are, measured, processed, looked at, and conveyed by practitioners of the discipline by having in mind first the classical-mechanics image of molecule vibration and rotation and after, with the advent of quantum mechanics, the electronic–vibrational–rotational scheme embodied in Eq. bo-(73). In other words, the CS-MDoF has always constituted the mental framework within which experimental spectroscopic evidence has been first interpreted and then described and applied. In this sense, spectroscopy as assimilated today is just an interpretative language based on the CS-MDoF. We are not entitled, therefore, to use the spectroscopy argument rearward to justify the presumed physical reality of the CS-MDoF. If we do so, we just introduce circularity and prove nothing. Let us try to understand better this point by means of an example. With the CS-MDoF in mind, experimenter C makes an emission-spectroscopy experience in which he is clever enough to tune up the experimental equipment to excite the gas molecules under conditions for which Eq. bo-(73) is applicable and to produce only (what he thinks in his mind to be) rotational-state transitions. Fortified in the Born–Oppenheimer approximation camp, he trusts the right-hand side of Eq. bo-(73) and he reports to have observed a transition

$$\Delta\left[\varkappa^4 W_{nsr}^{(4)}\right] = \varkappa^4 W_{ns(r')}^{(4)} - \varkappa^4 W_{ns(r'')}^{(4)} \tag{43}$$

from rotational state r' to rotational state r''. Experimenter N subscribes to the NS-MDoF. He processes the same data of the experiment performed by C in a different manner because the right-hand side of Eq. bo-(73) has no place in his mind. N simply reports that there has been a transition

$$\Delta W_{nsr} = W_{(nsr)'} - W_{(nsr)''} \tag{44}$$

from internal state $(nsr)'$ to internal state $(nsr)''$. Of course, from Eq. bo-(73), we can write

$$\Delta W_{nsr} = \Delta\left[\varkappa^4 W_{nsr}^{(4)}\right] \tag{45}$$

Thus, N is looking at the left-hand side of Eq. (45) and C is looking at the right-hand side of Eq. (45). Their quantitative statements agree. Therefore, there is no amount of theoretical or experimental funambulism that C can unsheathe from the reserve of his expertise to prove the rightness of CS-MDoF and the wrongness of NS-MDoF. It is just a matter of interpretation or language. However, N is in a better position than C because, when experimental circumstances move away from the domain of validity of the Born–Oppenheimer approximation [vicinity of the electronic-energy minimum; see Eq. bo-(40) in Fig. 3], his interpretation remains unshaken while C's interpretation fades hopelessly away together with the right-hand sides of Eqs. bo-(73) and (45).

The crucial macroscopic consequence of the conclusion drawn at the beginning of this section is embodied in Eq. (42): there is no physical soundness in speaking of or operating with electronic, vibrational, rotational contributions to thermodynamic properties. Within the context of the NS-MDoF, only translational and internal contributions are meaningful. Repercussions in parallel disciplines (gas-kinetics theory, chemical kinetics, thermal kinetics, state-to-state kinetics, radiation) are easily imaginable. Of course, we can choose, more or less consciously, to ignore the lesson and to go blindly ahead with the electronic–vibrational–rotational separation by morphing the $\neq$ sign in Eqs. (41) and (42) into an $=$ sign. But if we do so then we are only fabricating one of those physically illegal situations in which "… one artificially forces on the system one's preconceptions about behavior" as appropriately pointed out by Sutcliffe (p. 35 of [37]). Our disregard of the lesson implies the perpetration of a conceptual mistake, which is subtly more dangerous than a numerical mistake. The toll exacted by our conceptual mistake is that we end up dealing with properties, such as electronic, vibrational, and rotational temperatures (corresponding quantum-state population distributions as well), for example, that do not have significance in the physical reality and that should be at best considered as numerical conveniences, of the same kind of those magic coefficients which have been proliferating in turbulence models. We then proceed without hesitation to use the gradients of those numerical temperatures to calculate heat-flux contributions that build up a global flux [Eq. (6)] of poor accuracy and, in collaboration with uncertainties of other nature, constrain the sizing of spacecraft heat shields to compromise with the burden of safety margins that penalize payload mass.

The replacement of CS-MDoF with NS-MDoF constitutes an abrupt turn, of course, which requires a profound, although not drastic, rethinking of methods in theoretical and computational aerothermodynamics that have been established for a long time and are firmly ingrained in the mentality of practitioners of the discipline. Prospects of change in long-time established procedures induce hesitation by default. Yet the outcome of our quantum-mechanics investigation on the subject matter speaks loud and clear because it rests on solid conceptual foundations that appear not easily prone to demolishment. Indeed, there are already exploratory attempts [47] in that direction. We have to become accustomed with the NS-MDoF framework and make an effort to endorse it in thermochemical-nonequilibrium aerothermodynamic flow solvers in operation to produce heat-flux data fed into the design of spacecraft thermal-protection shields. In this regard, an important aspect to carefully study pertains to the behavior of population distributions over the internal quantum states. We must understand if and when those distributions have nonanalytical nature because, under those circumstances, recourse to state-to-state internal kinetics is unavoidable. On the other hand, under circumstances in which the populations turn out to be analytical (Boltzmann [13], Treanor et al. [48]) in nature, we will probably be in good shape to characterize thermal disequilibrium with translational and internal temperatures. (Although not crucial in context of the present discourse, there are still important conceptual problems in demand of resolution in the statistical thermodynamics of multitemperature gas mixtures. Details can be found in Secs. 2.8–2.10 of [11].)

Support from the physical-chemistry (theoretical and computational) and experimental-spectroscopy communities is vital in connection with the mentioned turn of course. The positive note is that quantum chemists and molecular spectroscopists seem unanimous in agreeing [47] on the following fact: the repercussions in their disciplines from the more physically consistent characterization of internal-structure molecular energy (with concern to typical molecules in the atmospheres of Earth [49], Mars [50], Jupiter, etc.) do not imply conceptual difficulties but only computational difficulties in terms of producing molecular data necessary to construct the more reliable physical models needed in aerothermodynamics. Their assessment is that computational difficulties may certainly require time but they could be surmounted if sufficient efforts are invested by a well-coordinated network of computational laboratories.

In conclusion, do we aerothermodynamicists have a responsibility to make an effort to improve the state of the art of the subject matter? The opinion emerged from a recent expert gathering [47] contemplates a positive answer, ensuing from the recognition that there will always be space missions requiring planetary (re)entry and from the concordance that it is time to relinquish old practices of heat-shield design based on last-minute fixes and safety factors drawn from designer's experience. But if we take the challenge then we must be en garde: our effort must be invested with the awareness that the road to improvement is long and difficult and with the conviction that such a road must be walked without hurry and with reasoned care and circumspection to avoid the risk of wasting precious resources.

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