

## Chapter 2

# A Comment on the Question of Degeneracies in Quantum Mechanics

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**Abstract** The problem of degeneracies, descending from the Born-Oppenheimer (B-O) approximation serves as a “comeback backdoor” of the principle of complementarity, but on a much more subtle level. Quantum mechanics incorporates both mechanical and field theory features, which results in the well-known particle-wave aspects of complementarity. The degeneracy problem, however, prompts a new type of “property-object” complementary phenomena. This leads to serious consequences: Field theoretical methods, unlike mechanical ones, are incapable of separating the internal and the external degrees of freedom with respect to the centre of gravity, but on the other hand adapt relativistically in a natural manner very similar to the space-time formulas of Maxwell’s equations. The solutions of the quantum field equations, relativistic in the mentioned specific sense, yield singularities at symmetric points that correspond to the well-known B-O degeneracies giving the latter in actual fact a metaphysical attribute. However, Nature has in this case a more sophisticated method or *modus operandi* to avoid degenerations and to instigate symmetry violations.

In quantum mechanics, we often encounter degenerate states, which are authentic and experimentally detectable. The most famous case of degeneracy removal is the splitting of states under the influence of external electric or magnetic fields (Stark and Zeeman effects). On the other hand, we also often come across virtual degenerate states that are the product of a simplified Hamiltonian, which we usually have to choose due to the possibility of a realistic analytical solution when the total Hamiltonian does not directly provide such a solution. Since the step toward the answer exploit the principle of superposition, the simplified Hamiltonian may lead to non-existent fictional degenerations, which are eventually eliminated when taking the total Hamiltonian into consideration. This removal is either resolved in perturbation theory or in a non-perturbative approach based on multiconfigurational interaction.

Realistic degenerate states are mostly well defined and they do not therefore need to be considered further here. In contrast, in the case of so-called virtual degenerate

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states there are many unresolved questions. A typical example is the situation of degenerate states arising in connection with the use of the Born-Oppenheimer (B-O) approximation [1]. Since the wave function of the system of electrons and nuclei can be decomposed due to their small mass ratio  $m/M$  into

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}, \mathbf{R})\chi(\mathbf{R}) \quad (2.1)$$

we can separately solve the equations for the electron and the nuclear states. Quantization is carried out in a hierarchical manner: First the electron states are parametrically quantized at given internuclear distances  $\mathbf{R}$

$$H_e(\mathbf{R})|\psi(\mathbf{r}, \mathbf{R})\rangle = E_e(\mathbf{R})|\psi(\mathbf{r}, \mathbf{R})\rangle \quad (2.2)$$

after which the introduction of the kinetic energy of electrons,  $T_e$ , the electron-nuclear and two-electron potentials,  $E_{eN}$  and  $E_{ee}$ , respectively, the electron Hamiltonian  $H_e$  in Eq. (2.2) is expressed as

$$H_e = T_e(\mathbf{r}) + E_{eN}(\mathbf{r}, \mathbf{R}) + E_{ee}(\mathbf{r}). \quad (2.3)$$

Finally the nuclear motions are quantized as

$$H_N|\chi(\mathbf{R})\rangle = E|\chi(\mathbf{R})\rangle \quad (2.4)$$

where one obtains for the nuclear Hamiltonian in Eq. (2.4) ( $T_N$  is the kinetic energy of nuclei and  $E_{NN}$  the internuclear potential)

$$H_N = T_N(\mathbf{R}) + E_{NN}(\mathbf{R}) + E_e(\mathbf{R}). \quad (2.5)$$

When Eq. (2.2), at the nuclear equilibrium position, causes a degenerate solution, represented by the crossing of two or more potential surfaces, the Jahn-Teller (J-T) effect [2] shows up. The usual responses to this impasse are the incorporation of standard non-adiabatic corrections as the only cure capable of removing the degeneracies originating from the B-O approximation.

There would be no further reason to think about the origin of this type of degeneracies, if field theoretic methods did not exist. In the latter situation, with an approach, borrowed from quantum electrodynamics and made operational within quantum mechanics and furthermore widely used in the theory of solids, we are in fact facing a similar degeneracy problem, but with a completely different method of solution regarding degeneracy removal. Perhaps the most famous is the model field Hamiltonian

$$H = \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} (b_{\mathbf{q}}^+ b_{\mathbf{q}} + 1/2) + \sum_{\mathbf{k}, \mathbf{q}, \sigma} u^{\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) a_{\mathbf{k}+\mathbf{q}, \sigma}^+ a_{\mathbf{k}, \sigma}. \quad (2.6)$$

Now the question arises how Eq. (2.6) relates with the B-O approximation. Electron and electron-phonon terms come from the second quantization of Eq. (2.3) neglecting the two-electron term, i.e.  $T_e + E_{eN}$ . The phonon term comes from the

second quantization of the B-O equation (2.5), i.e.  $T_N + E_{NN} + E_e$ . This means that whenever the system is in a degenerate situation in a quantum mechanical description, according to Eq. (2.2), it is simultaneously degenerate in the quantum field description, see to Eq. (2.6). What is indeed striking is the way the quantum mechanical approach on the one hand and the field theoretical approach on the other hand, in reality are capable to eliminate the degeneracy. The mechanical approach leads to multiconfigurational interaction descriptions including all intersecting potential surfaces, as is standard practice in the theory of J-T effect [3, 4], while the field theoretical approach uses the Fröhlich transformation [13] (which, unfortunately, is unable to remove the degeneracies) and subsequently the Bogoljubov-Valatin transformation [5], the latter reflecting the BCS theory [6], as is customary in the theory of superconductivity. Both approaches lead to broken symmetries. Again we find here a striking difference: the mechanical approach of the J-T effect leads to a structural symmetry breaking, whereas symmetry violations in the field theoretical approach to BCS theory relates to charge superselection rule violation.

At this point, we may correctly speculate over the differences between the two approaches, quantum mechanical and quantum field theoretical ones, and in particular over the origin of these differences as, e.g., resulting from the B-O approximation, and moreover how to completely bypass this almost undefeatable approximation. It provides a certain type of virtual degeneracies, and therefore the question appears whether these are still justified and if there exists some higher principle, that would entirely circumvent such circumstances and arrive without more ado at the desired lifting of the degeneration.

Actually, there is an, in principle, exact formulation in quantum mechanics, considered by Monkhorst [7, 8], which ignores the B-O approximation, but, however, suffers some disadvantages. Firstly, it is not possible to derive analytic expressions for quantum mechanical measurable quantities, cf. the B-O separation procedure; and secondly, even with the best computers the computations are numerically exceedingly demanding. It is in effect prohibiting even going beyond such a humble endeavour as just about ten considered particles, electrons and nuclei included. Hence, unfortunately, it is quite impossible to consider systems where the B-O approximation leads to electronically degenerated states, such as those leading to the J-T effect or the mechanisms of superconductors.

Regarding quantum field methods, there do not seem to exist any definite techniques in consideration of how to construct a field that is not based on the B-O approximation, or in other words going further than the model Hamiltonian (2.6). This Hamiltonian representation has turned out to be especially advantageous in treating systems like insulators and conductors, but alas in superconductivity it points to the same problems in analogy with non-adiabatic corrections in the J-T problem, i.e. one obtains B-O degenerate states that we then try to eliminate in a subsequent treatment.

The primary problem of the B-O approximation is related to the centre-of-mass (COM) notion. It was indeed one of the main reasons why Monkhorst promoted his concept and entirely avoided to make this approximation. However, it also appears that the mistake to determine the centre of gravity in the B-O approximation may be

compensated via the Born-Huang (or Born-Handy) [9, 10] ansatz, which provides the lowest diagonal adiabatic correction to the B-O formulation. The Born-Handy ansatz has been tested numerous times, and it yields accurate results in agreement with experiment. The reason behind the popularity of the Born-Handy ansatz and why it has been so carefully verified was its approximate avoidance of the COM problem in the B-O separation. Handy's contribution consisted, in addition to formulating the procedure, in convincing the broad scientific community of the value of this pragmatic ansatz, without having to solve the full COM problem, which amongst other things demands the introduction of relative coordinates and masses. Kutzelnigg then gave the proof that the Born-Handy ansatz fully replaces the very complicated and difficult COM solution [11].

Unfortunately, there exists no analogy of the Born-Handy ansatz in the field theoretical equation (2.6), which would compensate for the error in the determination of the centre of mass by means of the B-O approximation. If we perform its generalization for systems without translational symmetry (applicable not only to crystals with translational symmetry but also to molecules), and subsequently applying the Fröhlich transformation (cf. Fröhlich's attempts to explain superconductivity [13]), we obtain, for the ground state of the hydrogen molecule, only about 20 % of the total adiabatic correlation energy, while, in quantum mechanics, the Born-Handy ansatz yields the correct result [14, 15]. Of course, insulators or conductors are not as sensitive to these effects, and there we prevail with Eq. (2.6). Nevertheless, cf. non-adiabatic effects in connection with superconductivity, we have to devote deeper thoughts to the correctness of the Hamiltonian representation (2.6).

As we proceed we will look in more detail at the COM separation problem as it appears in the B-O approximation. Equation (2.4) leads to a solution in terms of coupled oscillators, in which relative coordinates represent normal coordinates of the vibrational modes. After introducing the normal coordinates  $B_r = b_r + b_r^+$  and  $\tilde{B}_r = b_r - b_r^+$  for the kinetic and potential energies, respectively, of the nuclei in the effective field of the electrons, we have

$$H_{BO} = E_{kin}(\tilde{B}) + E_{pot}(B) \quad (2.7)$$

where the kinetic and potential energies are given by

$$E_{pot} = \frac{1}{4} \sum_{r \in V} \hbar \omega_r B_r^+ B_r \quad (2.8)$$

$$E_{kin} = \frac{1}{4} \sum_{r \in V} \hbar \omega_r \tilde{B}_r^+ \tilde{B}_r. \quad (2.9)$$

From the B-O separation we finally get the well-known vibrational Hamiltonian

$$H_{BO} = \frac{1}{4} \sum_{r \in V} \hbar \omega_r (B_r^+ B_r + \tilde{B}_r^+ \tilde{B}_r) = \sum_{r \in V} \hbar \omega_r (b_r^+ b_r + 1/2). \quad (2.10)$$

The mechanical approach, based on this procedure, clearly separates the internal and the external degrees of freedom. The internal degrees correspond to vibrational

modes  $r$ ,  $r \in V$ , and the external degrees are reflected in the translational degrees of freedom corresponding to the de Broglie wave of COM, and the rotational degrees of freedom corresponding to the quantized states of angular momentum, with eigenvalues of  $L^2$  and  $L_3$ . An error in the determination of the centre of gravity is then entirely compensated by the Born-Handy ansatz, but only on the adiabatic level, as Kutzelnigg did prove [11].

The field theoretical approach, unfortunately, involves Eq. (2.10) as an ingredient in the total Hamiltonian (2.6) without any possibility to compensate for the COM factual error. Where is, however, the mistake? Is the error to be found in Eq. (2.10)? In considering this question, we get back to one of the fundamental problems of quantum mechanics, which for inexplicable reasons were never brought up for consideration. As is well-known, in quantum mechanics the mechanical and the field attributes are brought together, and this gives rise to recognized microscopic peculiarities, *viz.* the complementarity between the coordinate and the momentum representations, the alleged dualism of the considered entities, e.g., the appearance as particles or as waves, the non-commutativity between different classes of operators. Even if this has been correctly formulated for single-particle states, the general role of complementarity in quantum mechanics is not completely unraveled in this way. There is yet another manifestation of complementarity, which shows up at the many-body level, i.e. the degenerate states in the B-O many-body approximation just emerge as the reappearance through the backdoor of the fundamental principle of complementarity, however on a much more subtle level.

Equations (2.8) and (2.9) represent the standard quantum mechanical picture of vibrations as the properties of the system of electrons and nuclei. However, if we want to further include Eq. (2.10) in the ensuing field Hamiltonian (2.6), the vibrations must not be interpreted as properties only, but instead they are quantum mechanical objects themselves, ontologically equivalent with electrons. Hence, the external degrees of freedom cannot be separated from the internal ones, rather they are materialized in the form of quasiparticles, i.e. rotons and translons, cf. the internal degrees of freedom that are materialized e.g. in the form of phonons. This leads to a surprising deduction: Eqs. (2.8) and (2.9) have two mutually exclusive interpretations: firstly, they are the determining equations for the properties of electrons and nuclei, e.g. vibrations with a clear separation from the external degrees of freedom; or secondly, they are the generic equations for new quasiparticles, e.g. phonons, rotons and translons. In the latter case Eqs. (2.8) and (2.9) have the following solution:

$$E_{pot} = \frac{1}{4} \sum_{r \in V} \hbar \omega_r B_r^+ B_r \quad (2.11)$$

$$E_{kin} = \frac{1}{2} \left( \frac{1}{2} \sum_{r \in V} \hbar \omega_r + \sum_{r \in R} \rho_r + \sum_{r \in T} \tau_r \right) \tilde{B}_r^+ \tilde{B}_r. \quad (2.12)$$

Dual interpretations of the same equations with two alternate solutions, in the form of (2.8), (2.9) and (2.11), (2.12), result in a new type of complementarity.

Hence, in addition to the well-known particle-wave dualism, we discern here a new type of property-object dualism. Equations (2.11), (2.12) thus become the proper opening from the original mechanical formulation of the system of electrons and nuclei to the new field theoretic formulation of electrons, phonons, rotons and translons. There is here no reduction of the system into a subsystem with  $3N - 5(6)$  degrees of freedom, as in the B-O case, but we must instead consider all  $3N$  degrees, and as a replacement for vibrations, we introduce the concept of hypervibrations (vibrations + rotations + translations) and the corresponding hypervibrational double-vector

$$\omega = \begin{pmatrix} \omega_r \\ \tilde{\omega}_r \end{pmatrix} = \begin{pmatrix} \omega_r & 0 & 0 \\ \omega_r & \frac{2}{\hbar}\rho_r & \frac{2}{\hbar}\tau_r \end{pmatrix} \quad (2.13)$$

from which we get covariant expressions for the boson hypervibrational Hamiltonian with respect to all  $3N$  hypervibrational modes.

$$H_B = \frac{1}{4} \sum_r (\hbar\omega_r B_r^+ B_r + \hbar\tilde{\omega}_r \tilde{B}_r^+ \tilde{B}_r). \quad (2.14)$$

It is important to point out that this hypervibrational Hamiltonian (2.14), and not merely the vibrational Hamiltonian (2.10) must be used in the field equations of type (2.6). Consequently, while the mechanical pattern in quantum mechanics retains the classical separation of the degrees of freedom, the field theory pattern does not permit this, while binding together the internal and the external degrees in a relativistic manner. It may sound astonishing, but it looks like the second time in the history of physics, when we come across something similar. The space-time theory of relativity works in four-dimensions where the time can be seen as the fourth—external degree of freedom. This feature was not present in the classical mechanical laws of Newton, but it was finally discovered in the classical field equations known as Maxwell's equations, where the Lorentz transformation binds together space and time.

Although the property-object complementarity as well as the related relativistic nature of the degrees of freedom was not previously shown, Fröhlich, nevertheless, used the incomplete field Hamiltonian (2.6) and applied his transformation [13]

$$H' = e^{-S(Q,P)} H e^{S(Q,P)} \quad (2.15)$$

which refers only to the internal degrees of freedom. However, by attempting to remove the degeneracy in Eq. (2.6), and further, to get from the initial conducting state to the state of superconductivity the treatment fails since it would not produce the requisite gap. On the other hand we can generalize the Fröhlich transformation, and, instead of the ordinary vibrational modes, we will use the relativistic hypervibrational ones and in addition consider a general case without any translational symmetry requirement.

The following application, in accord with (2.15), of the two quasiparticle transformations, the first  $Q$ -dependent

$$\bar{a}_P = \sum_Q c_{PQ}(B) a_Q, \quad \bar{b}_r = b_r + \sum_{PQ} d_{rPQ}(B) a_P^\dagger a_Q \quad (2.16)$$

with the unitary conditions

$$\sum_R c_{PR}(B) c_{QR}^\dagger(B) = \delta_{PQ}, \quad d_{rPQ} = \sum_R c_{RP}^\dagger(B) [b_r, c_{RQ}(B)] \quad (2.17)$$

and the second  $P$ -dependent

$$\bar{a}_P = \sum_Q \tilde{c}_{PQ}(\tilde{B}) a_Q, \quad \bar{b}_r = b_r + \sum_{PQ} \tilde{d}_{rPQ}(\tilde{B}) a_P^\dagger a_Q \quad (2.18)$$

with the unitary conditions

$$\sum_R \tilde{c}_{PR}(\tilde{B}) \tilde{c}_{QR}^\dagger(\tilde{B}) = \delta_{PQ}, \quad \tilde{d}_{rPQ} = \sum_R \tilde{c}_{RP}^\dagger(\tilde{B}) [b_r, \tilde{c}_{RQ}(\tilde{B})] \quad (2.19)$$

will lead to new systems of fermions and bosons. The diagonalization procedures permit choosing an optimal system, where we achieve a realistic separation into individual (quasi) fermions and bosons with minimal interaction between them.

Looking at this problem from the standpoint of group theory, we realize that we must adhere to the Poincaré group, as one of the most general group reflecting the full symmetry of special relativity, a problem seldom treated in full generality. Asking the question what would the most general group be that reflects the full symmetry of the Fröhlich transformation, or in other words, what would be the analogy of the Poincaré group for transformations carried out in the field theoretic methods of quantum mechanics. It can be shown that the Fröhlich transformation in Eq. (2.15) is decomposable into a product of two quasiparticle transformations: the coordinate (adiabatic) and the momentum (non-adiabatic) ones. We can perform the generalization to the case without the implied translational symmetry in a very simple way by replacing the quasimomentum/spin notation, which Fröhlich used in his original work, by the spinorbital notation. A further simple generalization can also be attempted, given that the quasiparticle transformations remain valid, by replacing the vibrational modes  $r, r \in V$  by the hypervibrational modes  $r, r \in \{V, R, T\}$ .

We can now show that (2.16), (2.18) form a group. First we write their inverse transformations:

$$a_P = \sum_Q \bar{c}_{PQ}(\bar{B}) \bar{a}_Q, \quad b_r = \bar{b}_r + \sum_{PQ} \bar{d}_{rPQ}(\bar{B}) \bar{a}_P^\dagger \bar{a}_Q \quad (2.20)$$

$$a_P = \sum_Q \tilde{\bar{c}}_{PQ}(\tilde{\bar{B}}) \tilde{\bar{a}}_Q, \quad b_r = \bar{b}_r + \sum_{PQ} \tilde{\bar{d}}_{rPQ}(\tilde{\bar{B}}) \tilde{\bar{a}}_P^\dagger \tilde{\bar{a}}_Q. \quad (2.21)$$

It is easy to prove, see e.g. [17], that (2.16), (2.20) contain two invariants: the coordinate operator  $B$  and the number of fermion particles  $N$

$$\bar{B}_r = B_r, \quad \bar{N} = \sum_P \bar{a}_P^+ \bar{a}_P = \sum_P a_P^+ a_P = N \quad (2.22)$$

and further, the transformations (2.18), (2.21) contain also two invariants: the momentum operator  $\tilde{B}$  and the number of fermion particles  $N$

$$\tilde{\bar{B}}_r = \tilde{B}_r, \quad \bar{N} = \sum_P \bar{a}_P^+ \bar{a}_P = \sum_P a_P^+ a_P = N. \quad (2.23)$$

Finally, the transformations (2.16), (2.18) and their inverses (2.20), (2.21) are tied up in a certain way:

$$\bar{c}_{PQ}(\bar{B}) = c_{QP}^+(B), \quad \bar{d}_{rPQ}(\bar{B}) = - \sum_{RS} c_{PR}(B) d_{rRS}(B) c_{QS}^+(B) \quad (2.24)$$

$$\tilde{\bar{c}}_{PQ}(\tilde{\bar{B}}) = \tilde{c}_{QP}^+(\tilde{B}), \quad \tilde{\bar{d}}_{rPQ}(\tilde{\bar{B}}) = - \sum_{RS} \tilde{c}_{PR}(\tilde{B}) \tilde{d}_{rRS}(\tilde{B}) \tilde{c}_{QS}^+(\tilde{B}). \quad (2.25)$$

Consequently we realize that (2.16), (2.18) actually form a group and thus all systems of fermions and bosons, obtained by these are equivalent. It is the most general group of transformations of the Fröhlich type. Unfortunately the Fröhlich treatment was sadly undervalued and it is now primarily remembered as an ad hoc transformation that Fröhlich applied to the Hamiltonian describing conductors, while the resulting Hamiltonian was eventually used in the BCS theory of superconductivity. However, from the generalized group structure it follows, that Fröhlich type transformations are of cardinal importance, not only in solids, but also generally in quantum chemistry, where they are regrettably still practically unused. In conclusion we point out that the main interest lies in that this generalized group combines the internal and external degrees of freedom in a relativistic fashion.

As is quite obvious the present understanding only needs a straightforward knowledge of the quantum nature of the harmonic oscillator. As an example we investigate how the harmonic oscillator manifests itself in a different way comparing the mechanical, see (2.8), (2.9), and in the field approach, see (2.11), (2.12). Hence we immediately arrive at the novel type of complementarity as based on the property-object dualism. Continuing further with the degrees of freedom, where they, in classical form, enter directly in the electron-nuclear Hamiltonian. As a result of the COM formulation, they represent the quantum form of vibrational, rotational and translational quanta—as quasiparticles, which transform according to the most general group (2.16), (2.18). In the mechanical method one does not recognize any translational quanta, but the in the field theoretical case one does! It is not possible to separate internal and external degrees of freedom in the field formulation in contrast to the mechanical approach, and therefore we attain a new kind of relativistic flavour in molecular and solid state structures. This variety of relativity is logically



of quantum origin! Again, as already pointed out, all the aforementioned statements are merely a consequence of the properties of the harmonic oscillator.

Let us now continue by applying the general transformations, (2.16), (2.18), to the field Hamiltonian. Here we will only sketch the derivation, since it is, however, very time-consuming. The final formula for the change of the ground state energy has a surprisingly simple analytical form. Details of the derivation have been given in previous work [15] as well as a more comprehensive discussion in [16].

For the correction of the ground state energy we finally get

$$\Delta E_0 = \sum_{AIr} (\hbar\tilde{\omega}_r |c_{AI}^r|^2 - \hbar\omega_r |\tilde{c}_{AI}^r|^2) \quad (2.26)$$

where the summation refers to virtual spinorbitals  $A$ , occupied spinorbitals  $I$ , and all hypervibrational modes  $r$ ,  $r \in \{V, R, T\}$ . The coefficients  $c$  resp.  $\tilde{c}$  are related to the adiabatic and the non-adiabatic transformation, respectively, and determined by the set of equations

$$u_{PQ}^r + (\varepsilon_P^0 - \varepsilon_Q^0)c_{PQ}^r + \sum_{AI} [(v_{PIQA}^0 - v_{PIAQ}^0)c_{AI}^r - (v_{PAQI}^0 - v_{PAIQ}^0)c_{IA}^r] - \hbar\omega_r \tilde{c}_{PQ}^r = \varepsilon_P^r \delta_{PQ} \quad (2.27)$$

$$(\varepsilon_P^0 - \varepsilon_Q^0)\tilde{c}_{PQ}^r + \sum_{AI} [(v_{PIQA}^0 - v_{PIAQ}^0)\tilde{c}_{AI}^r - (v_{PAQI}^0 - v_{PAIQ}^0)\tilde{c}_{IA}^r] - \hbar\tilde{\omega}_r c_{PQ}^r = \tilde{\varepsilon}_P^r \delta_{PQ} \quad (2.28)$$

where  $u$  are the coefficients of the electron-hyperphonon interaction,  $\varepsilon^0$  are one-electron energies, and  $v^0$  two-electron potential energies.

For the derivation we stress the most interesting three limits of Eq. (2.26):

- (a) The adiabatic limit, which means that all non-adiabatic coefficients  $\tilde{c}$  will be equal to zero. Thus, we obtain the adiabatic correction

$$\Delta E_{0(ad)} = \sum_{AIr} \hbar\tilde{\omega}_r |c_{AI}^r|^2 = 2 \sum_{AI} \left( \sum_{r \in V} \frac{1}{2} \hbar\omega_r + \sum_{r \in R} \rho_r + \sum_{r \in T} \tau_r \right) |c_{AI}^r|^2 \quad (2.29)$$

which we can directly compare with the Born-Handy ansatz. In the author's works [14, 15], the exact CPHF reformulation of the Born-Handy ansatz is displayed, leading to the identity between the field and the mechanical equations at the adiabatic level

$$\Delta E_{0(ad)} = \langle \psi(\mathbf{R}) | T_N | \psi(\mathbf{R}) \rangle_{R_0} = 2 \sum_{AI} \left( \sum_{r \in V} \frac{1}{2} \hbar\omega_r + \sum_{r \in R} \rho_r + \sum_{r \in T} \tau_r \right) |c_{AI}^r|^2. \quad (2.30)$$

Numerical verification was performed on the molecules  $H_2$ ,  $HD$  and  $D_2$  [14]. It was surprising that the vibrational contribution only amounted about 20 %,

while the remaining 80 % consisted of rotational and translational contributions, even if considering molecules at rest, i.e. they neither rotate nor move. This comparison is very important because the field equations used in the theory of solids and derived from the B-O approximation, kept only the first term in (2.30), which is in complete contrast to the Born-Handy ansatz. From the identity of (2.29) and (2.30), we can clearly see how the mechanical and the field approaches get by differently with the inaccurate determination of the centre of gravity, however, eventually leading to the same results, i.e. that the mechanical Born-Handy ansatz is equivalent to the relativistic field correction.

- (b) The non-relativistic limit + neglect of the two-electron terms. It means that the summation in Eq. (2.26) will involve only the internal degrees of freedom—phonons.

$$\Delta E_0 = \sum_{AI, r \in V} (\hbar\omega_r |c_{AI}^r|^2 - \hbar\omega_r |\tilde{c}_{AI}^r|^2) = \sum_{AI, r \in V} |u_{AI}^r|^2 \frac{\hbar\omega_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2 - (\hbar\omega_r)^2} \quad (2.31)$$

from which, after changeover from quantum chemical to solid state physics notation, we get exactly the same results as originally derived by Fröhlich [12, 13].

$$\Delta E_0 = 2 \sum_{\mathbf{k}, \mathbf{k}'; \mathbf{k} \neq \mathbf{k}'} |u^{\mathbf{k}' - \mathbf{k}}|^2 f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) \frac{\hbar\omega_{\mathbf{k}' - \mathbf{k}}}{(\varepsilon_{\mathbf{k}'}^0 - \varepsilon_{\mathbf{k}}^0)^2 - (\hbar\omega_{\mathbf{k}' - \mathbf{k}})^2}. \quad (2.32)$$

Unfortunately, as mentioned above, this equation did not acquire the expected superconducting gap, as Fröhlich initially had expected. In fact the optimization of the occupation factors  $f_{\mathbf{k}}$  yields some decrease of the total energy and Fröhlich then tried to interpret this new state as the superconducting state.

- (c) The complete non-adiabatic and relativistic limit, where we only omit two-electron terms in order to obtain transparent analytical expression:

$$\Delta E_0 = \sum_{AIr} |u_{AI}^r|^2 \frac{\hbar\tilde{\omega}_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2 - (\hbar\omega_r)^2} \quad (2.33)$$

which in the form of the sum of vibrational, rotational and translational parts finally reads

$$\begin{aligned} \Delta E_0 = & \sum_{AI, r \in V} |u_{AI}^r|^2 \frac{\hbar\omega_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2 - (\hbar\omega_r)^2} \\ & + 2 \sum_{AI, r \in R} |u_{AI}^r|^2 \frac{\rho_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2} + 2 \sum_{AI, r \in T} |u_{AI}^r|^2 \frac{\tau_r}{(\varepsilon_A^0 - \varepsilon_I^0)^2}. \end{aligned} \quad (2.34)$$

After the rewriting Eq. (2.34) in solid state notation we obtain

$$\begin{aligned} \Delta E_0 = & 2 \sum_{\mathbf{k}, \mathbf{k}'} |u^{\mathbf{k}'-\mathbf{k}}|^2 \frac{\hbar \omega_{o, \mathbf{k}'-\mathbf{k}}}{(\varepsilon_{c, \mathbf{k}'}^0 - \varepsilon_{v, \mathbf{k}}^0)^2 - (\hbar \omega_{o, \mathbf{k}'-\mathbf{k}})^2} \\ & + 4 \sum_{\mathbf{k}, r \in R} |u^r|^2 \frac{\rho_r}{(\varepsilon_{c, \mathbf{k}}^0 - \varepsilon_{v, \mathbf{k}}^0)^2} + 4 \sum_{\mathbf{k}, r \in T} |u^r|^2 \frac{\tau_r}{(\varepsilon_{c, \mathbf{k}}^0 - \varepsilon_{v, \mathbf{k}}^0)^2} \quad (2.35) \end{aligned}$$

where  $o$  denotes the optical branches and  $c, v$  the conducting and the valence bands respectively.

Equations (2.34), (2.35) are indeed quite intriguing. Here degenerate states cannot exist unless all the matrix elements of electron-roton and electron-translon interactions are equal to zero. If not, these types of interactions induce singularities in symmetric points, where the system would be degenerate according to the B-O approximation. Rotons and translons thus cause symmetry breaking, which results in automatic elimination of system degeneracies. Degenerations resulting from the B-O approximation therefore constitute a metaphysical trait, as well as do the concepts of intersecting potential surfaces.

Unfortunately, many scientists consider real and virtual degeneracies to be of the same nature, as well as their removal, and that the J-T effect and superconductivity should be treated on an equal footing using the same quantum mechanical rules as e.g. the Stark and the Zeeman effects. As we have seen here this is not true. Nature has yet another, more sophisticated means to eliminate virtual degenerations, and not removing them in some perturbative or multiconfigurational way as usually carried out in the case of realistic ones.

The question arises how to interpret the B-O approximation, which entrusts a metaphysical essence to the resulting degeneracies. The development of quantum mechanics due to the practical but misleading B-O paradigm has somehow stalemated halfway between the mechanical and field theoretical methods, and exactly at the unlucky point where the corresponding complementarity cannot be seen at the same time leading to incorrect metaphysical conclusions. As a possible recipe the author recommends either to go back, totally ignoring the B-O procedure, like was done by Monkhorst in his concept which in fact is the only correct mechanical approach, or to go on to the concluding line, where the relativistic field approach ultimately appears. Despite some incongruousness's as regards the theory of special relativity, cf. the fulfillment of the group properties of the Poincaré group, the latter will not be fully solved until we have obtained a consistent quantum gravity theory.

Quantum mechanics is today considered to be a closed discipline; that means, it should not lead to any internal contradictions. As we have shown here, in this work, the transformed standard field Hamiltonian, compared with the Born-Handy ansatz, yields the same paradox as if trying to apply the Galilean transformation to Maxwell's equations. The only way out of this quantum mechanical crisis is to incorporate the concept of a relativistically noncontradictory structure of molecules and crystals, binding together their internal and external degrees of freedom in the same way as the Lorentz transformation binds together space and time. We then arrive at the more general concept of relativity principles, which concern explicitly internal and external degrees of freedom. Relativity of space and time forms

a special subclass, in which the three internal (spatial) and one external (time) coordinates are bound into a four-dimensional spacetime. Brändas recently opened a discussion of the possible quantum origin of Einstein's general relativity [18].

Here we have described a different subclass of relativity considerations, with reference to the structure of molecules and crystals, which follows as a direct result of the overlooked property-object dualism. The particle-wave dualism is not the only manifestation of Bohr's complementarity; there is also a more subtle property-object dualism. In conclusion we refer to the old controversy between Einstein and Bohr, with Einstein's answer to the puzzles of quantum mechanics: "God does not play dice." Thus we can understand the principle of relativity as a direct consequence of the general complementarity principle.

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## References

1. Born M, Oppenheimer R (1927) *Ann Phys (Leipzig)* 84:457
2. Jahn HA, Teller E (1937) *Proc R Soc London A* 161:220
3. Köppel H, Domcke W, Cederbaum LS (1984) *Adv Chem Phys* 57:59
4. Bersuker IB (2006) *The Jahn-Teller effect*. Cambridge University Press, Cambridge
5. Bogoliubov NN (1958) *Nuovo Cim* 10 Ser 7:794
6. Bardeen J, Cooper LN, Schrieffer JR (1957) *Phys Rev* 108:1175
7. Monkhorst HJ (1987) *Phys Rev A* 36:1544
8. Cafiero M, Adamowicz L (2004) *Chem Phys Lett* 387:136
9. Born M, Huang K (1954) *The dynamical theory of crystal lattices*. Oxford University Press, London
10. Handy NC, Lee AM (1996) *Chem Phys Lett* 252:425
11. Kutzelnigg W (1997) *Mol Phys* 90:909
12. Fröhlich H (1950) *Phys Rev* 79:845
13. Fröhlich H (1952) *Proc R Soc Lond A* 215:291
14. Svrček M, Baňacký P, Biskupič S, Noga J, Pelikán P, Zajac A (1999) *Chem Phys Lett* 299:151
15. Svrček M (2012) In: *Progress in theoretical chemistry and physics*, vol 22. Springer, Berlin, pp 511–552. Part 7
16. Svrček M (2012). [arXiv:1207.0711](https://arxiv.org/abs/1207.0711) [physics.gen-ph]
17. Svrček M (1992) In: *Molecular vibrations. Methods in computational chemistry*, vol 4. Plenum, New York, pp 150–202 (Chap 2-6.2) & pp 204–229 (Chap 7)
18. Brändas E (2009) *Frontiers in quantum systems*. In: Russo N, Antonchenko VYa, Kryachko E (eds) *Chemistry and physics. NATO science for peace and security series A: chemistry and biology*, vol 18. Springer, Dordrecht, pp 49–87

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