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The complete symmetrization of quantum operators: new thoughts on an old problem*

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The complete symmetrization with respect to $x, p_x, \ldots$ of the operators associated with dynamical properties can sometimes lead to results different from those obtained by the conventional quantum formalism based on the rule $\mathrm{op}\,(A^2) = (\mathrm{op}\,A)^2$. For example, angular momentum operators M_z^2 and M^2 are modified by the additive constants $\hbar^2/2$ and $3\hbar^2/2$ respectively ($M^2 \neq 0$ for electron in the ground state of H atom, rotator never at rest, but spectra unchanged); the average quadratic dispersion of energy is different from zero. These results can be interpreted by assuming that the system is never strictly isolated but communicates with the other systems of the universe by means of electromagnetic interactions. Quantum mechanics would give only average values over a sufficiently long time and would exhibit a quasi-ergodic character. Examples supporting this possibility are given, in particular that of arsines for which quantum forecasts correspond to average values over one year.

Key words: Interpretation of quantum mechanics — Quantum operators

Introduction

Constructed initially to account for experimental observations, quantum mechanics has become a formalism whose physical meaning is sometimes difficult to discern. The basic idea on which quantum mechanics is built is that, to any classical dynamical property $G(p, q)$, there corresponds a linear operator $\hat{G}$ such

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

that the result of the measurement of G belongs to the spectrum of $\hat{G}$. Since the results of physical measurements are real, $\hat{G}$ must be *self-adjoint.* This condition is often replaced by the weaker condition that $\hat{G}$ must be *Hermitian*, which is sufficient to ensure that the average value of the observable is real.

The problem of the construction of the operators certainly remains a difficult fundamental question in quantum mechanics. The elementary rule given in most quantum mechanics textbooks, namely that the operators $\hat{G}$ are obtained directly from the corresponding classical expressions $G(p, q)$ by replacing the components $p_u (u = x, y, z)$ of the momentum of each particle in the expression of G by the corresponding operators $\hbar/i\, \partial/\partial u$, i.e.

$$\hat{G}(u, p_u) = G\left(u, \frac{\hbar}{i}\frac{\partial}{\partial u}\right) \tag{1}$$

is not sufficient. Indeed, in general, the operators thus obtained are not even Hermitian owing to the fact that $\hat{u}$ and $\hat{p}_u$ do not commute.

In 1927 Schrödinger [1] proposed to replace qp^2 by $qpp + ppq$, pqp or $(qpp + pqp + ppq)/3$ before building the corresponding operator. Subsequently, various solutions have been proposed for $q^n p^m$, always based on a preliminary more or less complete symmetrization of the classical expression with respect to the cartesian variables q and p [2–7]. For instance, p^2q^2 is replaced by $(p^2q^2 + q^2p^2)/2$ or after complete symmetrization [6] by

$$(qqpp + qppq + ppqq + qpqp + pqpq + pqqp)/6. \tag{2}$$

In fact, such quantities $q^n p^m$ appear in expressions arising from the square of dynamical properties G^2 so to ensure the self-adjointness condition it has been customary to put

$$\text{op}\,(G^2) = (\hat{G})^2. \tag{3}$$

More generally, for the product AB of two dynamical properties, conventional quantum mechanics utilizes the following rule

$$\text{op}\,(AB) = (\hat{A}\hat{B} + \hat{B}\hat{A})/2. \tag{4}$$

Unfortunately, this manner of proceeding leads to the following unacceptable consequence known as Temple's paradox [8]: according to (4), three operators, $((\hat{A}\hat{B})\hat{C})$, $((\hat{A}\hat{C})\hat{B})$, $((\hat{B}\hat{C})\hat{A})$ correspond to the product of three properties A, B, C. These operators are different unless the operators $\hat{A}$, $\hat{B}$, $\hat{C}$ commute, i.e., $\hbar = 0$. The complete symmetrization with respect to q and p as in (2) removes the paradox, as then only one operator, indeed, corresponds to ABC, even if $\hat{A}$, $\hat{B}$, $\hat{C}$ do not commute. This is, of course, logically more satisfying. It may therefore be useful to examine the consequences of such a symmetrization in a detailed manner with the object of seeing whether its consequences are acceptable or are inconsistent with experiment. That is the aim of this paper.

Operators associated with M_z^2 and M^2

The operators associated with M_z^2 and with

$$M^2 = M_x^2 + M_y^2 + M_z^2 \tag{5}$$

can be constructed according to two completely different procedures. If we adopt (3), we must write

$$\operatorname{op}(M^2) = (\hat{M}_x)^2 + (\hat{M}_y)^2 + (\hat{M}_z)^2 = \hat{\mathfrak{M}}^2. \tag{6}$$

On the contrary, if we start from the classical expression, after complete symmetrization (sym), we obtain [9]

$$\operatorname{op}(M_z^2)_{\text{sym}} = (\hat{M}_z)^2 + \frac{\hbar^2}{2} \tag{7}$$

and

$$\operatorname{op}(M^2)_{\text{sym}} = (\hat{M}_x)^2 + (\hat{M}_y)^2 + (\hat{M}_z)^2 + \tfrac{3}{2}\hbar^2 = \hat{\mathfrak{M}}^2 + \tfrac{3}{2}\hbar^2. \tag{8}$$

The operators (7) and (8) are self-adjoint, and their eigenfunctions are the same as those of $(\hat{M}_z)^2$ and $\hat{\mathfrak{M}}^2$ respectively. These operators commute with $\hat{M}_z$ and with the Hamiltonian $\hat{H}$ in the case of atoms (the spin-orbit interaction being neglected) so that all the results concerning the classification of the atomic levels are unchanged. The only difference concerns the value of M^2. For instance, for the ground state of the hydrogen atom, M^2 is equal to $\frac{3}{2}\hbar^2$ while the conventional quantum formalism gives zero. Intuitively, the value $\frac{3}{2}\hbar^2$ seems to be more rational than the conventional value given the motion of the electron. In this connection, it is interesting to recall that, to remove this difficulty, Dirac [10] proposed $\hat{\mathfrak{M}}^2 + \hbar^2/4$ for the operator associated with M^2.

Another consequence of the complete symmetrization is that, even in the case where ψ is eigenfunction of $\hat{M}_z$ and $\hat{M}^2$, the values of M_z and M^2 are not constant: e.g.

$$(\Delta M_z)^2 = \frac{\hbar^2}{2}. \tag{9}$$

Consequently, for the plane rotator, we obtain

$$(\Delta M_z)(\Delta\varphi) = \frac{\pi\hbar}{\sqrt{6}} = 0.72\hbar. \tag{10}$$

In the conventional formalism, the Heisenberg relationship

$$(\Delta M_z)(\Delta\varphi) \geq \hbar/2 \tag{11}$$

fails to be true [11] given $\Delta M_z = 0$. Again the complete symmetrization appears to be more satisfactory than the orthodox formalism.

Moreover, the plane rotator is never at rest. The corresponding zeropoint rotational energy is equal to $\hbar^2/4I$, all the levels being shifted by this same additive quantity, so that its spectrum is unchanged. Likewise for an unsymmetrical top, the corresponding shift is $(1/I_X + 1/I_Y + 1/I_Z)\hbar^2/4$ (I_X, I_Y, I_Z = principal moments of inertia).

Operator associated with E^2

The square of the energy appears when one considers the quadratic dispersion of the energy $(\Delta E)^2$. If we adopt the conventional formalism from (3) we have

$$\mathrm{op}\,(E^2) = (\hat{H})^2 \tag{12}$$

so that $(\Delta E)^2$ is equal to zero for all the eigenstates. If however we start from the completely symmetrized expression for E^2 we obtain a dispersion different from zero. The case of the harmonic oscillator is typical in this regard [7]. From (2b) we obtain

$$\mathrm{op}\,(E^2)_{\mathrm{sym}} = (\hat{H})^2 + \frac{k}{4m}\hbar^2 \tag{13}$$

(m being the mass of the oscillator, and k its force constant) so

$$(\Delta E)^2 = \frac{k}{4m}\hbar^2 \neq 0. \tag{14}$$

More generally, for a particle whose potential energy is U, we obtain [9]

$$(\Delta E)^2 = \frac{\hbar^2}{4m}\langle\psi \cdot \nabla^2 U \cdot \psi\rangle. \tag{15}$$

Consequently, it follows from the previous equations that the energy does not remain constant, but fluctuates as a function of time about the corresponding eigenvalue of $\hat{H}$. This outcome is inconsistent with the hypothesis that the system is isolated. It corresponds to a coupled subsystem.

In fact, the true problem is to know what meaning must be given to the label "isolated". The theory of measurement affords an example which clearly shows the complexity of this notion. According to the orthodox interpretation, during a measurement, the system interacts with the measurement apparatus. Thus the system is not strictly isolated and its energy fluctuates when it is in presence of a device. Therefore, it is not unreasonable to take into account a *continuing* interaction between the system and its surrounding.

The first idea which comes to mind concerning the nature of this interaction, is that it is electromagnetic in origin. As far back as 1924, Slater [12] wrote "Any atom may, in fact, be supposed to communicate with other atoms, by means of a virtual radiation field". The first attempt at an explicit calculation seems to have been the Stochastic Electrodynamics (SED) [13]. This theory assumes that the electrons are subjected, on the one hand, to the Lorentz damping force, and, on the other (to compensate for the loss of energy), to a random electromagnetic field which fills the whole universe. Within this model energy fluctuates. The results obtained from SED for the harmonic oscillator are in complete agreement with the quantum results. However SED results are inconsistent with quantum results for other systems [14].

SED does not make the origin of the background field precise [13]. Nonetheless, it is reasonable to imagine that this field arises from the radiation of all the systems which constitute the universe [15]. Such a hypothesis has to be compared with the Wheeler–Feynman absorber theory [16]. However, the introduction of the half-retarded and half-advanced fields of the latter theory into the framework of SED makes the energy dispersion vanish for stationary states [17].

Up to now, the idea of the balance between the radiated and absorbed powers for an "isolated" system immersed within the field created by the other systems of the universe, has not been formulated in a satisfying manner by any classical theory. Although the idea is exciting, the mathematical difficulties are presently too great for definitive conclusions to be obtained.

A compatibility condition between classical and quantum physics

A measurement is never instantaneous so that its result is the average value, over the time of the measurement, of the property being observed. Consequently, the result can depend on the duration of the observation. The example of Newton's disk is typical in this regard. It appears to us as white and at rest if the rotation is sufficiently rapid (say 50 Hz), whereas a photo using a very brief time-exposure (0.001 s) distinctly shows the various colored sectors and successive photos allow us to detect the rotation.

If the electron remains a particle in the hydrogen atom, given that its average kinetic energy is different from zero, we must admit that it is moving and that, if no experiment is able to detect its motion, we are in a case comparable with the visual observation of Newton's disk. In other words, since quantum mechanics agrees with experiment, its forecasts would correspond to a time-average over a sufficiently long observation time. The stability of the results versus time would signify that the underlying dynamics exhibits an *ergodic* (more precisely *quasi-ergodic*) character [18]. Let τ_e be the ergodicity time, i.e. the minimum time necessary to obtain stable time-average values, and τ_m, the duration of the measurement. Then the system exhibits the quantum character only if $\tau_m \gg \tau_e$.

As a first example, let us consider the H_2^+ ion. At the elementary LCAO-MO level, the molecule possesses two electronic states respectively symmetric, ψ_S, and antisymmetric, ψ_A. The oscillation period T of a wave-packet between the two nuclei is equal to h/E^*, E^* being the transition energy between ψ_S and ψ_A [19]. In so far as T can be used as an order of magnitude for τ_e, we obtain the following results. At the equilibrium distance, ($R_0 \sim 2$ a.u.), $\tau_e \sim 10^{-16}$ s; for $R = 40$ a.u., $\tau_e \sim 1$ s, and for $R = 60$ a.u., $\tau_e \sim 5$ years. In other words, the notion of molecule would be vanishingly small for large internuclear distances. This would be very satisfying for the chemist. The fact that τ_e for electrons in molecules ($\sim 10^{-16}$ s) is 10^4 times smaller than the one for molecular vibration ($\sim 10^{-12}$ s) gives a physical meaning to the Born–Oppenheimer approximation. The quantum electron density is reached much more quickly than the density corresponding to the vibrations.

The pyramidal molecules MXYZ afford another typical example. These compounds exist in two inverse forms of opposite handedness which are able to change into one another more or less quickly. Theoretically, the problem is that of a particle within a symmetrical double-well potential. The quantum ground state corresponds to a symmetrical density with two maxima localized above the two wells respectively. Such a state does not exhibit any optical activity. The two inverse forms (D and L) which the chemist would expect to find appear to have no physical existence [20]. Experiment shows that amines (M = nitrogen) do not exhibit rotatory power and are not able to be resolved into D and L isomers. Phosphines (M = phosphorus) and arsines (M = arsenic), however, are resolvable. In addition if we start from a certain quantity of a given isomer (e.g. D), the substance progressively *racemizes* (i.e. is changed into a mixture containing equal amounts of the D and L forms), thus becomes optically inactive. One month is necessary for obtaining this transformation for phosphines, and one year for arsines [21]. This means that, if we were able to observe one molecule and to draw the histogram of its properties, the quantum distribution would be reached only after a sufficiently long time. For amines, $\tau_e \sim 10^{-12}$ s and for arsines $\tau_e \sim 1$ year. This is a proof of the physical reality of the two enantiomeric forms although they are unobservable in the case of amines. In amino acids, the racemization time is 10^5 years and this phenomenon is used in paleontology for absolute dating of fossil bones [22]. The reversible interconversion $D \rightleftarrows L$ can be explained in a classical way by the more or less easy jump over the potential barrier between the two wells. The fluctuations in energy allow the system to acquire sufficient energy to pass over the barrier without us being constrained to admit the tunneling effect.

Other examples of systems for which the ratio τ_e/τ_m is important can be quoted. The instantaneous picture obtained from absorption spectra of transition metal compounds differs strongly from the pictures obtained from techniques with a larger characteristic time-scale (e.g. X-ray crystallography) [23]. Similarly, electron diffraction indicates that the octofluorocyclobutane C_4F_8 exhibits the symmetry V_d (with all angles equal to 109.5° and the cycle folded along one of the two diagonals (4 equivalent structures are possible)), while infra-red spectroscopy suggests this molecule is planar (D_{4h}) with all the angles being equal to 90° [24]. The cycle oscillates from one V_d structure to another passing through the D_{4h} planar form. The maximum quantum density corresponds to the V_d structures which appear in an electron diffraction experiment whose duration is extremely long with respect to the oscillation period. The infra-red spectrum is a faster time scale measurement and, consequently, the lines corresponding to the D_{4h} structure appear.

A difficulty, nevertheless, remains concerning the absorption spectra. Quantum mechanics forecasts spectra made up of infinitely sharp lines whose frequencies are determined by the differences between the corresponding eigenvalues of $\hat{H}$. This seems to be incompatible with a dispersion in energy for the eigenstates. In fact, the absorption lines exhibit a finite breath showing that the problem is more complex. The absorption could be an extremely sharp resonance without connection to the dispersion in energy. Besides, SED offers an example (namely that of the harmonic oscillator) where the spectrum is discrete while the energy fluctuates [13].

A possible molecular test

Since the consequences we have drawn so far from the complete symmetrization procedure concern only the *interpretation* of the quantum formalism, it may seem that the problem is purely academic. However, with the accuracy of present day experimental methods and theoretical *ab-initio* methods, it may be possible to find the answer to this question through the examination of molecular properties which depend on a possible zero-point contribution of the rotational energy.

For instance, according to Eq. (8), the zero-point energy of a diatomic molecule is equal to

$$\varepsilon_0 = \hbar^2/4I = \hbar^2/4\mu R_e^2 \tag{16}$$

μ being the reduced nuclear mass and R_e the equilibrium internuclear distance. As examples, one finds $\varepsilon_0 = 3.5$ meV for H_2 and 0.02 meV for O_2 at their respective equilibrium distances [25]. For the separated atoms ($R = \infty$), $\varepsilon_0 = 0$, so that the dissociation energy D_0 should be correspondingly decreased by ε_0. Since $\varepsilon_0 = D - D_0$, where D is the vibro-electronic and D_0 the experimental dissociation energy, a test of the value of ε_0 requires very accurate experimental measurements of D_0 and very accurate *ab-initio* calculations of D. The latter are within reach for small molecules. The former are more delicate since the determination of dissociation energies is based on the extrapolation of the vibrational energy levels with respect to anharmonicities and rotation-vibrational interactions. This extrapolation procedure would also have to be modified to account for ε_0 decreasing with higher vibrational excitations. Nonetheless, in principle the possibility for future tests exists.

Conclusion

We can summarize the consequences of complete symmetrization of operators with respect to the position coordinates x, y, z, and the corresponding momenta p_x, p_y, p_z, as follows:

(i) A certain number of logical difficulties are removed including Temple's paradox and the Heisenberg uncertainty relationship for the rotator.

(ii) Although the physical outcomes which arise from the symmetrization are different from those which are conventionally admitted, they are not inconsistent with experiment and are in some sense more rational. For examples, $M^2 \neq 0$ in $H(1s)$, and similar to an oscillator, a rotator is never at rest.

(iii) The fluctuations for all dynamical properties, which are the most important consequence of the symmetrization, may lead to a quasi-ergodic interpretation of quantum mechanics, the (classical or quantum) behavior of the system depending on the value of the ratio τ_m/τ_e. The system is not strictly isolated but exchanges energy with all the systems which constitute the universe.

(iv) High accuracy experiments and *ab-initio* calculations in the field of chemical physics may provide a resolution to the symmetrization question which had been left unsettled since the 1930s.

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References

1. Schrödinger E (1927) Ann Physik 79:734
2. Weyl H (1931) The theory of groups and quantum mechanics. Dutton, New York
3. Moyal J E (1949) Proc Cambridge Phil Soc 45:99
4. Margenau H, Hill R N (1961) Proc Theoret Phys (Kyoto) 26:722
5. Born M, Jordan P (1925) Z Phys 34:873
6. Boyer T H (1975) Phys Rev D11:809
7. Castellani L (1978) Il Nuovo Cimento 48A:359
8. Temple G (1935) Nature 135:957
9. Julg A, Julg P (1979) Folia Theoret Chim Latina 7:63
10. Dirac P A M (1947) The principles of quantum mechanics, 3rd edn. Clarendon Press, Oxford, p 144
11. Judge D (1963) Phys Letters 5:189; Judge D, Lewis J T (1963) Phys Lett 5:190; Harris R A, Strauss H L (1978) J Chem Educ. 55:374
12. Slater J C (1924) Nature 113:307
13. See for instance: Boyer T H (1975) Phys Rev D11:790; Claverie P, Diner S (1977) Int J Quant Chem XII, suppl 1:41 (numerous references)
14. Julg P (1979) Folia Theoret Chim Latina 6:99; Pasquera L, Claverie P (1982) J Math Phys 23:1315
15. Marshall T W (1963) Proc Royal Soc (Lond) 276A:475; Julg A (1980) La liaison chimique. Presses Universitaires, Paris
16. Wheeler J A, Feynman R P (1945) Rev Mod Phys 17:157; (1949) 21:425
17. Imaeda K, Imaeda M (1982) J Phys A: Math Gen 15:1243
18. Blanc-Lapierre A, Casal P, Tortrat A (1959) Méthodes mathématiques de la mécanique statistique. Masson, Paris
19. Eyring H, Walter J, Kimball G E (1944) Quantum chemistry. Wiley, New York
20. Julg A (1984) Croat Chim Acta 57:1497
21. Costain C C, Sutherland G B M (1952) J Phys Chem 56:321; Weston R E (1954) J Am Chem Soc 76:2645
22. Julg A, Lafont R, Périnet G (1987) Quaternary Sci Rev 6:25
23. Jørgensen C K (1971) Modern aspects of ligand theory. North-Holland, Amsterdam
24. Lemaire H P, Livingston R L (1950) J Chem Phys 18:569; Edgell W, Weiblen D G (1950) J Chem Phys 18:571
25. Huber P, Herzberg G (1979) Molecular spectra and molecular structure, IV. Constants of diatomic molecules. van Nostrand-Reinhold, Princeton