Comment on "On the product of noncommuting quantum observables," by E. Kapuscik [Am. J. Phys. 56, 230–231 (1988)]

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(Received 27 September 1988; accepted for publication 24 January 1989)

In a recent short article[1] it was claimed that the symmetrized product of noncommuting quantum observables (the Weyl rule) should be rejected because it is not compatible with the "canonical quantization" procedure (i.e., Dirac's proposal of assigning commutators to Poisson brackets).

It is impossible to take exception to the assertion that "the symmetrized product ... is not compatible with the canonical quantization procedure." But the conclusion to be drawn should be, I believe, the opposite of Kapuscik's. It is widely recognized nowadays that the "canonical quantization" procedure is not consistent for big enough sets of observables (for instance, the set of all polynomials in the canonical variables), at least if one adds natural requirements, such as linearity. If it were otherwise, the Poisson structures of classical and quantum mechanics would be identical, which, of course, is not the case. The proof was given by van Hove[2] many years ago and by now has found its way into the textbooks.[3,4]

[1] E. Kapuscik, Am. J. Phys. **56**, 230 (1988).
[2] L. van Hove, Mem. Acad. R. Belg. **XXVI**, 61 (1951).
[3] R. Abraham and J. E. Marsden, *Foundations of Mechanics* (Benjamin, Reading, MA, 1978).
[4] V. Guillemin and S. Sternberg, *Symplectic Techniques in Physics* (Cambridge U.P., New York, 1984).

A new derivation of the particle density formula in quantum mechanics

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(Received 1 July 1988; accepted for publication 25 January 1989)

Consider a system of N particles with coordinates X_1, $X_2,...,X_N$ described by a spatial wavefunction Φ. The average number of particles in any region Ω in three-space R^3 is given by,

$$\langle n\rangle = \int_\Omega \sigma(X)dX, \tag{1}$$

where,

$$\sigma(X) = N\int_{(R^3)^{N-1}} |\Phi(X,X_2,X_3,...,X_N)|^2 \times dX_2\, dX_3...dX_N, \tag{2}$$

and we have used the notational abbreviation

$$\int_{R^3} dX_i = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx_i\, dy_i\, dz_i,$$

Equation (1) has numerous important applications in both physics and chemistry.[1-11] It is the basis of population analysis in quantum chemistry[3,4] and is implicit in the definition of the one-particle density matrix.[5] In crystallography, $\langle n\rangle$ is measured experimentally as the electron density function. Furthermore, analogs of Eqs. (1) and (2) arise in the statistical theory of liquids.[6,7] In this latter context, if the N particles are described by a potential U and partition function Z, then the average number in Ω is given by Eq. (1) with σ replaced by

$$\sigma(X) = N\int_{(R^3)^{N-1}} Z^{-1}\exp[-\beta U(X,X_2,X_3,...,X_N)] \times dX_2\, dX_3...dX_N, \tag{3}$$

where $\beta = 1/kT$ is the Boltzmann factor. Although intuitively reasonable, it is not completely obvious that Eq. (1) should yield the mean number of particles as expressed by the fundamental definition of the first moment, namely,

$$\langle n\rangle = \sum_{i=0}^{N} iP(i)\left(\sum_{i=0}^{N} P(i)\right)^{-1} = \sum_{i=0}^{N} iP(i), \tag{4}$$

where $P(i)$ is the probability of finding exactly i particles in region Ω. If the particle locations were independent, the result would follow from the formula for the mean of a binomial distribution. However, electrons are correlated so

that the number of electrons in a volume Ω is certainly not a binomial random variable.

Typical textbook derivations[5–11] of Eq. (1) have the pedagogical disadvantage of not utilizing explicitly the fundamental definition (4). In addition, many contain errors of a probabilistic nature. References 8 and 9, for example, consider the case $N=2$ and assume that the probability of finding an electron in some volume dV is the sum of the probability that electron 1 is in dV given that electron 2 is anywhere and the probability that electron 2 is in dV given that electron 1 is anywhere. While it is true that probability theory allows for the addition of probabilities for disjoint events, it does not permit the addition of conditional probabilities that are conditioned against different events. The result of adding such probabilities does not in general yield a probability density. By confusing the concepts of number density and probability, this type of proof in effect assumes the statement that is to be proved. Similar objections apply to the proofs given in Refs. 6, 7, and 10. Some texts[11] simply assume that the electron number density is the sum of the appropriate one-electron probability densities. Although intuitively reasonable, this is precisely the point at issue.

On the other hand, proofs of Eq. (1) may be obtained by subsuming the entire topic into the general theory of density matrices.[12] However, it would seem to be of much greater pedagogical value to obtain (1) from first principles and later use it as motivation for the definition of the one-particle density matrix.

The objective of this article is to present an alternative proof of (1). It is completely elementary using only the definition of the mean number as expressed by Eq. (4), together with the standard statistical interpretation of the wavefunction.

We begin by noting that the probability of finding exactly i particles in a region Ω is given by

$$P(i) = \binom{N}{i} P(X_1 \in \Omega, X_2 \in \Omega, \ldots, X_i \in \Omega, X_{i+1} \notin \Omega \ldots, X_N \notin \Omega).$$

This follows from the fact that, by antisymmetry of the wavefunction, the (marginal) probability density function of any subset of i particles is identical to the density function of the first i particles. Furthermore, there are exactly $\binom{N}{i}$ such subsets. Next, by the statistical interpretation of the wavefunction, we can write

$$P(i) = \binom{N}{i} \int_{\Omega^i} \int_{(\Omega^c)^{N-i}} |\Phi|^2 \, dX_1 \, dX_2 \ldots dX_N,$$

where Ω^c is the complement of Ω in R^3. In this equation, the first i coordinates are integrated over the region Ω and the remaining $N-i$ over its exterior. At this point we deviate from the usual derivations and substitute for $P(i)$ directly in the definition of the mean number, Eq. (4). Noting that

$$i\binom{N}{i} = N\binom{N-1}{i-1},$$

we obtain

$$\langle n \rangle = N \sum_{i=1}^{N} \binom{N-1}{i-1} \int_{\Omega^i} \int_{(\Omega^c)^{N-i}} |\Phi|^2 \, dX_1 \, dX_2 \ldots dX_N. \tag{5}$$

In the case $N=3$, Eq. (5) reduces to

$$\langle n \rangle = 3 \int_{\Omega} \left(\iint_{\Omega^c \times \Omega^c} |\Phi|^2 \, dX_2 \, dX_3 + 2 \iint_{\Omega \times \Omega^c} |\Phi|^2 \, dX_2 \, dX_3 + \iint_{\Omega \times \Omega} |\Phi|^2 \, dX_2 \, dX_3 \right) dX_1.$$

But

$$\begin{aligned}(R^3)^2 &:= R^3 \times R^3 \\ &= (\Omega \cup \Omega^c) \times (\Omega \cup \Omega^c) \\ &= (\Omega \times \Omega) \cup (\Omega \times \Omega^c) \cup (\Omega^c \times \Omega) \cup (\Omega^c \times \Omega^c).\end{aligned}$$

Furthermore, by antisymmetry of Φ, the integral over $\Omega \times \Omega^c$ is identical to the integral over $\Omega^c \times \Omega$. Hence

$$\begin{aligned}\langle n \rangle &= 3 \int_{\Omega} \left(\int_{(\Omega \cup \Omega^c)^2} |\Phi|^2 \, dX_2 \, dX_3 \right) dX_1 \\ &= 3 \int_{\Omega} \left(\int_{(R^3)^2} |\Phi|^2 \, dX_2 \, dX_3 \right) dX_1 \\ &= \int_{\Omega} \sigma(x) dX,\end{aligned}$$

which was to be proved. The general case is equally simple. A shift in the range of summation in Eq. (5) yields

$$\langle n \rangle = N \int_{\Omega} \sum_{i=0}^{N-1} \binom{N-1}{i} \times \int_{\Omega^i} \int_{(\Omega^c)^{N-1-i}} |\Phi|^2 \, dX_1 \, dX_2 \ldots dX_N.$$

Now this equation has a number of features in common with the binomial theorem. Using this fact and the case $N=3$ as a guide, it is easy to verify that it reduces to

$$\begin{aligned}\langle n \rangle &= N \int_{\Omega} \int_{(\Omega \cup \Omega^c)^{N-1}} |\Phi|^2 \, dX_1 \, dX_2 \ldots dX_N \\ &= N \int_{\Omega} \left(\int_{(R^3)^{N-1}} |\Phi|^2 \, dX_2 \, dX_3 \ldots dX_N \right) dX_1 \\ &= \int_{\Omega} \sigma(X) dX.\end{aligned}$$

Finally, to prove the corresponding formula in statistical mechanics, we need simply replace $|\Phi|^2$ by $\exp(-\beta U)/Z$ in the above argument. The only modification required is to note that, in this case, equality of the one-particle marginal density functions follows from symmetry of the energy function U rather than from the antisymmetry of the wavefunction.

[1] R. G. Parr, in *Electron Distributions and the Chemical Bond*, edited by P. Coppens and M. B. Hall (Plenum, New York, 1982).

[2] Vedene H. Smith, Jr. and Ilyas Absar, "Basic Concepts of Quantum Chemistry for Electron Density Studies," Isr. J. Chem. **16**, 87–102 (1977).

[3] R. S. Mulliken, "Electronic Population Analysis on LCAO-MO wavefunctions I," J. Chem. Phys. **23**, 1833–1840 (1955).

[4] R. S. Mulliken, "Electronic Population Analysis on LCAO-MO wavefunctions II, Overlap Populations, Bond Orders, and Covalent Bond Energies," J. Chem. Phys. **23**, 1841–1846 (1955).

[5]R. Daudel, G. Leroy, D. Peeters, and M. Sana, *Quantum Chemistry* (Wiley, New York, 1983), pp. 130–135.
[6]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), pp. 180–184.
[7]D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976), pp. 257–258.
[8]R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry Methods and Applications* (Wiley–Interscience, New York, 1960), p. 62.
[9]R. McWeeny, *Spins in Chemistry* (Academic, New York, 1970), pp. 68–71.
[10]R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, London, 1969), pp. 76–78.
[11]D. B. Cook, *Structures and Approximations for Electrons in Molecules* (Ellis Horwood, Chichester, 1978), p. 37.
[12]R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975), pp. 57–64.

A simple demonstration of conduction in glass at high temperature

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(Received 14 October 1988; accepted for publication 19 February 1989)

As the temperature of glass is raised, more and more electrons contribute to electrical conduction. Unlike metallic conductors, which increase in resistance when they are heated, the glass can make the transition from very good insulator to conductor. In his classic book on demonstration experiments, Sutton[1] describes a dramatic demonstration of this transition. His method requires a fairly elaborate setup in which a glass rod, held in a special clamp, begins to conduct as its temperature is raised by means of a torch. I am suggesting here a much simpler demonstration that clearly shows the phenomenon but requires less equipment and preparation than Sutton's version.

Figure 1 indicates the equipment needed. A small piece of window glass (roughly $40\times15\times3$ mm) is held by two paper clips (the kind usually made from black, spring steel and opened by means of chrome-plated wire handles). Besides supporting the glass, the clips provide points for electrical connection. An insulating support for each clip can be a Pyrex rod stuck through the clip on one end and clamped to a ring stand on the other. The power is supplied by an ordinary 120-V ac outlet. Alligator clips provide easy attachment to the paper clips holding the glass.

The demonstration begins with the (bulb-shorting) switch open and the piece of glass in series with the bulb. (I usually use a 200-W bulb, but smaller bulbs will work.) A Bunsen burner or propane torch is used to heat the glass. It is important that the full clip-to-clip width of the glass be heated. As the glass begins to glow, close observation will reveal small sparks between the glass and the clips that hold it. With continued heating, the bulb should begin to glow, clearly indicating conduction by the glass. At this point, if the flame is removed, the glass will be heated by the current through it. This heating may not be sufficient to maintain the high temperature. However, if the bulb is then shorted out by the switch, the current will be larger. The glass will become hotter and brighter and will eventually melt and open the circuit. The bright final glow gives this demonstration a dramatic finish.

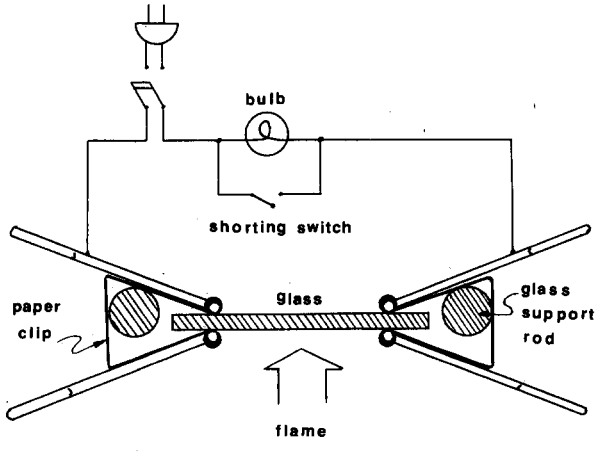

Fig. 1. Conduction-of-glass apparatus.

Each performance will require a new piece of glass and new paper clips. The old clips will be greatly weakened by the heat. Otherwise, the equipment is reusable.

Some precautions are in order. There is an obvious shock hazard with 120 V on exposed metal surfaces. Of course, the apparatus should be unplugged during setup and at any other time the demonstration is not in progress. Additional protection can be provided by a "dead-man" switch that disconnects the power when not held closed. I have equipped my power cord with a spring-loaded rocker switch that disconnects both wires when it is not held down. Because there may be some sputtering as the melting glass drips away, the audience and the demonstrator should be a safe distance away at this point. A Plexiglas shield between the molten glass and the audience is a good idea. The demonstrator should wear glasses or goggles. The table top should be protected from the molten glass by something that will not be ignited or damaged.

I hope this easily performed, inexpensive demonstration of conduction by glass at high temperatures will find application in solid-state and thermal physics classes as well as in introductory courses.

[1]Richard Manliffe Sutton, *Demonstration Experiments in Physics* (McGraw-Hill, New York, 1938), pp. 317–318.