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Reply to a Comment by Milonni on

"A Classical/Semiclassical Theory for the Interaction of Infrared Radiation
with Molecular Systems"

By

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I am happy to have this opportunity to expound further on the classical model I have proposed for describing the interaction of molecules with infrared radiation.

Regarding Milonni's first point, concerning my ascertion that "spontaneous submission is a totally classical phenomenon that has nothing to do with quantum mechanics", his arithmetic in the second paragraph of the comment is quite correct but his interpretation of it in the third paragraph misses its meaning: i.e., spontaneous emission resulting from the classical model can indeed be thought of as simply classical radiation from a time-dependent dipole, but this is precisely what spontaneous emission is, classically or quantum mechanically. The truth of this is evident from many points of view, perhaps the most straight-forward being to compare the expression for the classical spontaneous emission rate to the correct quantum expression, Eqs. (4.19) and (4.25) of reference 1: in terms of their respective

classical and quantum dipole correlation functions the two expressions are identical, which makes it rather obvious that the classical model is indeed describing the classical analog of the quantum process. Thus one way of "deriving" the classical expression for spontaneous emission would be to start with the quantum expression in terms of the quantum dipole correlation function, replace the quantum dipole correlation function by the classical one, and Q.E.D. One can then observe, as Milloni has, that the classical expression is simply classical radiation by a time-dependent dipole.

One of Milloni's difficulties seems to be (cf. his third paragraph) that he thinks the "transition moment connecting two energy eigenstates" has no classical analog. It is well-known, however, that matrix elements of the coordinate x , say, are directly related to the classical function $x_{CL}(t)$, i.e., the classical trajectory. For a harmonic oscillator, for example, with integer action variable n (i.e., in quantum state n) one has the classical expression

$$x_{CL}(n,t) = \sqrt{\frac{(2n+1)\hbar}{m\omega}} \cos(\omega t + \text{constant}) \quad , \quad (1)$$

and this is intimately related to the fact (via the Heisenberg correspondence relation²) that the matrix elements of x are

$$x_{n,n'} = \sqrt{\frac{(n+n'+1)\hbar}{m\omega}} \quad ,$$

$$n-n' = \pm 1 \quad . \quad (2)$$

The relation for a general anharmonic oscillator is

$$x_{n,n'} \approx [E'(n)/2\pi\hbar] \int_0^\tau dt x_{CL}(\frac{n+n'}{2}, t) \quad (3)$$

where $E(n)$ is the energy of the oscillator in terms of the classical action n (i.e., $E(n)$ is the WKB eigenvalue function) and τ is the vibrational period. One way to "derive" this well-known Heisenberg correspondence relation is simply to equate the classical and quantum autocorrelation functions,

$$\langle x(t) x(0) \rangle \quad ; \quad (4)$$

upon expanding the quantum expression by introducing intermediate sums over states, matrix elements $x_{n,n'}$ enter and the identification in Eq. (3) results.

Milloni's second point concerns my statement that absorption and induced emission balance each other in the completely classical ($\hbar \rightarrow 0$) limit. This is so clear and well-known³ that it hardly needs comment. The quantum expression for the net energy absorbed, for example, involves the imaginary part of the dipole correlation function, which is indeed non-zero quantum mechanically. Classically, however, the dipole correlation function is real and there is no net energy change. For the case of a Boltzmann distribution over molecular states it is possible to express the imaginary part of the dipole correlation function in terms of the real part,³ but here too the imaginary part vanishes as $\hbar \rightarrow 0$ (which is the standard way one always obtains the classical limit of quantum mechanics.⁴)

Finally, Milonni notes (cf. end of third paragraph) that over the years there have been "long standing debates over whether the quantum theory of radiation is required to properly describe the observed features of spontaneous emission". This was the reason, of course, I thought it interesting in reference 1 to point out how simply spontaneous emission appears in the classical model developed there. (The comments on spontaneous emission are mentioned only as an aside.) The basic reason the picture is so simple is that both molecule and radiation field are treated on the same dynamical footing, i.e., both by classical mechanics: Spontaneous emission is simply energy transfer between two coupled oscillators, the "molecule oscillator" which is initially excited and the "radiation field oscillator" that is initially unexcited. Classical mechanics is, of course, only an approximation to quantum mechanics, so the spontaneous emission rates computed from the classical formulae-- i.e., by using the classical dipole correlation function--will not in general give the exactly correct quantum values. (If the molecule is a harmonic oscillator, though, the classical result happens to be exact.) The point is that the process is described qualitatively correctly, and for molecular systems the description is even often quantitative.

Acknowledgments

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References

1. W. H. Miller, J. Chem. Phys. 69, 2188 (1978).
2. See, for example, W. H. Miller and C. W. McCurdy, J. Chem. Phys. 69, 5163 (1979).
3. See, for example, R. G. Gordon, Adv. Magn. Reson. 3, 1 (1968).
4. Cf. W. H. Miller, Adv. Chem. Phys. 25, 69 (1974).

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