molecular masses, respectively, k is the Boltzmann constant, and σ_e is the e–M elastic cross section taken as the hard sphere model.[2,10] In pure O_2 at $T = 300$ K with $1 \lesssim n_e \lesssim 10^7$ cm^{-3} and $n_{O_2} \gtrsim 10^{17}$ cm^{-3},[8] $s_{ee}/s_{eM} \lesssim 1$ and the hole-filling effect of the e–e collision may be comparable to that of the e–M elastic collision at the largest density ratio $n_e/n_{O_2} \simeq 10^{-10}$.

(7) For the attachment cross section with a much broader width (and a much smaller magnitude)[11] the attachment hole may be considerably smaller owing to the larger Maxwellization probability of an electron.

Finally, the following corrections should be made on p. 391 of Ref. 2: $J = 0, 2, 4, \ldots$ for $O_2 \rightarrow J = 1, 3, 5, \ldots$ for $O_2(^3\Sigma_g^-)$; $v_M/v_M/v \ll 1 \rightarrow v_M/v \ll 1$; $P_{MD}(v_M)$ in $\nu_B \rightarrow P_{MD}(\mathbf{v}_M)$; $p(\Omega) = \frac{1}{4}\pi \rightarrow 1/4\pi$; $Q = 0.3 \rightarrow -0.3$.

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Highly excited states of HCN: The probable applicability of classical dynamics

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The conclusion of Lehmann, Scherer, Klemperer[1] regarding the applicability of classical mechanics to the HCN problem is discussed further and several suggestions are made.

In a recent paper, Lehmann, Scherer, and Klemperer[1] suggest incompatibility of what they refer to as "stochastic" dynamics, as determined by calculation of classical power spectra,[2] and a highly regular experimentally observed spectrum (easily fit using perturbation theory), and conclude that classical mechanics is not applicable to the HCN problem. This presents an opportunity to make several observations.

The suggestion by Percival[3] of a close connection between classical chaotic motion (i.e., nonintegrable dynamics) and an *irregular* quantum spectrum has inspired both theoretical and computational explorations as to the possible nature of the quantum chaos expected to be associated with the classical chaos.[4] Zaslavskii[5] and Berry and Tabor[6] have discussed the statistics of expected neighbor level spacings for chaotic and quasiperiodic motion. McDonald and Kaufman[7] have calculated quantum spectra for a model problem which shows classical chaos, and obtained level spacings consistent with multiple avoided crossings, as predicted, see also Ref. 4. However, the Hamiltonian system of Ref. 7 is quite artificial in character when compared to those which model vibrations of actual molecules. The fact that nonanalytic (in the sense of Cauchy) model problems such as those of Ref. 7 and analytic model vibrational Hamiltonians (such as those of Henon–Heiles,[8(a)] Barbanis,[8(b)] and Thiele–Wilson[8(c)]) both show classical chaos suggests a possibly nonexistent similarity, which allows us to observe that *not all classical chaos is equivalent*: It is for this reason that chaotic (undefined but intuitively understandable) rather than stochastic (which has statistical implications) is prefered in describing the nonquasiperiodic trajectories. For example, the chaos of Ref. 7 is a classical C system,[9] i.e., has very strong statistical mixing properties involving exponentiation of neighboring trajectories. However, examination of the chaos on the three potential surfaces of Ref. 8, as carried out by Jaffé, Shirts, Hedges, and Reinhardt[10–12] indicates a surprisingly large amount of short to intermediate term regularity (up to hundreds of periods). We call such systems almost integrable (see also Ref. 13), and suggest that, even though their long time dynamics appears quite chaotic as determined by surface of section[4] or power spectrum techniques,[2] the chaos in such systems will often have no observable effect on quantum spectra. This led Jaffé and Reinhardt[10] to use perturbatively obtained approximate classical constants of motion to quantize all of the chaotic phase space for the Henon–Heiles problem, with excellent agreement with fully quantum results, leading to the conclusion that the presence of chaos was totally

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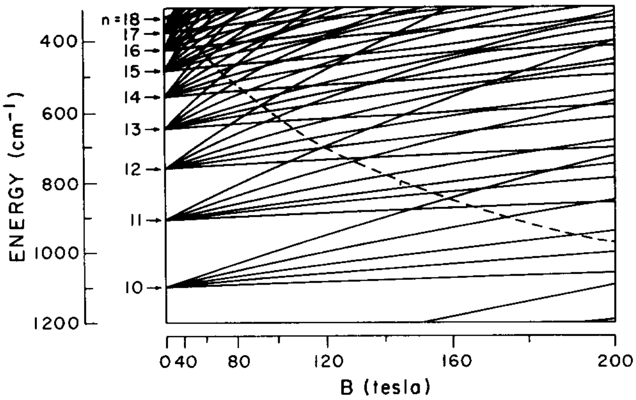

FIG. 1. Hydrogenic Zeeman energy levels as calculated variationally by Zimmerman *et al.* (Ref. 16) as a function of magnetic field in Tesla. At low field, or low n, the classical dynamics is quasiperiodic suggesting classical constants of motion analogous to the approximate quantum constants suggested in Ref. 16 following observations of many near level crossings. At high field or high n the classical dynamics is chaotic. The boundary between the quasiperiodic and chaotic regions of classical phase space is indicated by the dashed curve: one notes that most of the near crossings of the actual quantum levels persist well into the "chaotic" regime. More quantitatively, the size of the avoided crossings decreases as $e^{-\alpha n}$ (n = principal quantum number) in both the quasiperiodic and chaotic regions of classical regions, suggesting that tunneling rather than classical chaos determines the splittings.

irrelevant for the classical-quantum correspondence.[10] We strongly suspect that this is also the case for HCN, thus implying that it is only the *expectation* of a correspondence between classical chaos and irregularity of the quantum spectrum which led the authors of Ref. 1 to the conclusion that classical mechanics is inapplicable.

NKM have correctly pointed out that for the value of the coupling used by Jaffé and Reinhardt[10] there are no near-avoided crossings of quantum states, and thus potential ramifications of classical chaos might not have shown up.[4] However, the presence of classical chaos is not even necessarily directly associated with the magnitude of avoided crossings. Figure 1 shows quantum levels for Rydberg states of atomic hydrogen as a function of magnetic field strength. The hydrogenic Zeeman problem has the dual advantages that it is a physical problem (as compared to the model problems of Refs. 7 and 8) and that there is no doubt as to knowledge of the potential surface (see comments in Ref. 1 and in the following paper by Lehmann *et al.*). The classical dynamics for this quadratic Zeeman problem is chaotic at either high field or high energy, however quite good approximate classical constants have been found.[14,15] The levels of Fig. 1 were calculated by Zimmerman *et al.*,[16] and are essentially the exact quantum levels for the problem. The figure shows many apparent crossings of levels of the same symmetry. On higher magnification the quantum calculations show small avoided crossings, which are exponentially small in *both* the classically regular and chaotic regions: The magnitude of the crossings scales as $e^{-\alpha n}$ well into the chaotic regions.[16,17] This is in direct contradiction to the qualitative expectations of Gay[18] and of Robnik,[19] who, for probably the same intuitive reasons as the authors of Ref. 1, expected more strongly avoided crossings as the volume of chaotic phase space increased. Again we conclude that the existence of classical chaos apparently has nothing to do with the quantum spectrum. The fact that good approximate classical constants have been found[14,15] suggests that the Zeeman problem is almost integrable and also leads to the expectation that the whole of the spectrum of Fig. 1 may follow from integrable approximations to the dynamics, provided that an appropriate multidimensional uniform approximation is used.[20]

What, then, is needed, before inferences as to the possible effect of underlying classical chaos on quantum dynamics are drawn, is an as yet undiscovered quantitative measure of the strength—on a scale relevant to the size of Planck's constant—of that chaos. Perhaps the quantum Reynolds number recently introduced by Tabor[21] will provide such a measure. Without such a quantitative measure it is evident that mere observation of classical chaos does not provide sufficient reason for any conclusions as to the nature of the quantum spectrum.

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Response to 'Highly excited states of HCN: The probable applicability of classical dynamics'[a]

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The conclusion of our note on HCN[1] is in agreement with the conclusion of the comment by Farrelly and Reinhardt.[2] Farrelly and Reinhardt conclude that "the mere observation of classical chaos does not provide sufficient reason for any conclusion as to the nature of the quantum spectrum." This agrees with our conclusion that "the onset of classical chaos has no observable effect on the quantum mechanical eigenfunctions considerably above the stochastic transition for HCN." Their example of the hydrogenic Zeeman problem demonstrates the lack of quantum consequences of classical chaos in a completely calculable example. It is a problem that has physical relevance and the advantage of having a potential that is known. Unfortunately, its applicability to the understanding of vibrations of polyatomic systems is not clear.

Farrelly and Reinhardt conjecture that the HCN surface we used is "almost integrable" and so can be semiclassically quantized using approximate classical dynamics. We find this speculation reasonable, and certainly hope that these authors will determine if their speculation is correct. As discussed in our complete paper on HCN,[3] we attributed the lack of consequences of classical chaos to quantum mechanical smoothing over the small scale classical structure. It is believed that small, but overlapping classical resonances can cause chaotic motion.

Farrelly and Reinhardt's disagreement with our paper appears to be semantic. Our title refers to the inapplicability of classical dynamics since we believed that the HCN spectrum shows that classical chaos has no quantum consequences. Farrelly and Reinhardt believe that approximate classical mechanics can be used to semiclassically quantize, and conclude that classical dynamics is probably applicable. Semiclassical quantization is not classical dynamics. We find their usage somewhat misleading, given the extensive literature that exists speculating on the quantum consequences of classical chaos.

We would like to take this opportunity to report on some further work we have done on classical trajectories of HCN. We have run trajectories on two other potential surfaces for HCN: (1) the new surface recently reported by Murrell, Carter, and Halonen,[4] and (2) a coupled Morse potential, given in Table I. The expressions

TABLE I. Parameters for the coupled morse potential.

$$V(r_1, r_2) = V_{11} z_1^2 + V_{12} z_1 z_2 + V_{22} z_2^2 + V_{111} z_1^3 + V_{222} z_2^3$$

$$z_i = (1 - e^{-\alpha_i (r_i - r_i^0)})$$

r_1 = C–H bond length; r_2 = C–N bond length

$\alpha_1 = 1.84527$ Å^{-1} $\alpha_2 = 2.3062$ Å^{-1}

$V_{11} = 0.916877$ aJ[a]
$V_{12} = -0.04958$ aJ
$V_{22} = 1.7586$ aJ
$V_{111} = -0.0215$ aJ
$V_{222} = -0.0591$ aJ

[a]We apologize for the use of SI units.

TABLE II. Energy at which chaotic motion is first observed.

I. Carter, Mills, and Murrell[a]	16 469 cm^{-1}
II. Murrell, Carter, and Halonen[b]	43 945 cm^{-1}
III. Coupled Morse potential (see Table I)	31 150 cm^{-1}

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