nately, we were unable to measure this resonance with our present cw water laser.

The inversion process in laboratory water lasers is not known, but it no doubt involves selective excitation by collision. Possibly the same process operates in shock fronts or other locally dense and disturbed regions of interstellar gas, thereby powering type-I masers, but there is also a simpler laser inversion process that can account reasonably well for the main-line OH radiation from infrared stars. This is a radiative inversion, drawing its energy from the 2.8-$\mu$m blackbody radiation of the star and operating through the special properties of perturbed vibration-rotation energy levels in water vapor. The upper level of the 79.1-$\mu$m laser transition, because it is perturbed, has a much larger probability of excitation from the ground state by 2.8-$\mu$m radiation than does the lower level. The same holds for several other pairs of laser levels. Hence population inversions can be maintained in water vapor near an infrared star, and amplification of the star's radiation at 79.1 $\mu$m and other discrete wavelengths will result. Under saturated laser conditions, one 79.1-$\mu$m photon will be emitted for each 2.8-$\mu$m photon absorbed in lines that populate the upper laser level. Used in turn to pump the OH maser, each 79.1-$\mu$m photon will be converted to an 18-cm photon. With good geometry, correct velocities, and sufficient optical depth in the infrared absorptions, the overall efficienty of this process can be as much as 100 times greater than that of Litvak's near-infrared continuum pumping process.[1] The condition most difficult to satisfy may be that of sufficient optical depth, since the absorption coefficient of the magnetic-dipole pumping transition is 300 times smaller than that of the weakest pumping transitions in Litvak's scheme. For an OH region of given size and density the orders of magnitude cancel, and it is probably fair to say that the two pumping processes can have about equal efficiency.

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## MONOCHROMATIC RADIATION FROM A COHERENT MODULATED BEAM OF CHARGED PARTICLES

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It is suggested that intense laser fields may be used to modulate the wave functions of electrons. A classical model is used to demonstrate the greatly altered radiation fields of these electrons after they emerge from the laser beam. The observation by Schwarz and Hora of visible radiation from a nonluminescent target appears to result from these fields.

With the advent of laser techniques, it has become possible to modulate a particle beam at laser frequencies by a method similar to that employed in the conventional klystron. This rapid modulation introduces the possibility of observing effects associated with the longitudinal coherence length of individual particles. [This length is a measure of the size of a particle's wave packet in the direction of the beam.] If the pulse length in the modulated beam is long compared with the coherence length, the only possible effect of the modulation is the physical bunching of the particles in the beam; any subsequent radiation from them may be treated in the convention-

al manner. If the pulse length is short compared with the coherence length, then the wave functions of the individual particles themselves become modulated. However, at the usual laser power levels, no physical bunching takes place due to the fact that the increment in velocity imparted to the particle by the laser field is small compared with the spread of the velocities in the beam. Therefore, the only possible effects arise from the modulation of the wave function. Figure 1 is a schematic diagram of wave function for the case where there are three pulses within the coherence length of a single particle. The modulating frequency becomes an intrinsic property of the wave functions and the radiation associated with the beam during any subsequent process is markedly altered. Thus, observable effects should be seen in synchrotron radiation, bremsstrahlung, Cherenkov radiation, scattering processes, etc. According to a classical model, which we use below, the frequency distribution of the radiation field is modified in a simple manner by the modulation.

The model used for a particle is a wave train of length $L$ whose motion can be described in terms of a classical trajectory. The displacement of a fixed point in the wave train measured along the trajectory is given by $S(t)$. Let $F(t)$ be the current as a function of time at a point on the trajectory specified by $s=0$. If the spreading of the packet can be neglected, the same current occurs at any other point on the trajectory with a suitable time delay. The current is then given by

$$j(s,t)=F(t-\tau(s)), \tag{1}$$

where $\tau$ is the inverse function of $S$, and we have chosen $\tau(0)=0$. Equation (1) may be rewritten in the form

$$j(s,t)=\int dt' F(t')v(s)\delta(s-S(t-t')), \tag{2}$$

where

$$v(s)=[d\tau(s)/ds]^{-1}, \tag{3}$$

and may be interpreted as the velocity of a particle at point $s$. The charge density is then

$$\rho(s,t)=\int dt' F(t')\delta(s-S(t-t')). \tag{4}$$

It follows that the electric field at some observation point $\vec{x}$ is given by

$$\vec{E}(\vec{x},t)=\int dt' F(t')\vec{E}_p(\vec{x},t-t'), \tag{5}$$

where $\vec{E}_p(\vec{x},t)$ is the electric field which would be created by a point particle with unit charge whose motion is the same as any fixed point on the wave train. The field $\vec{E}_p(\vec{x},t)$ may be calculated from the Lienard-Wiechert potentials for the particular trajectory in question, and will lead to the usual radiation pattern for the process involved (e.g., bremsstrahlung).

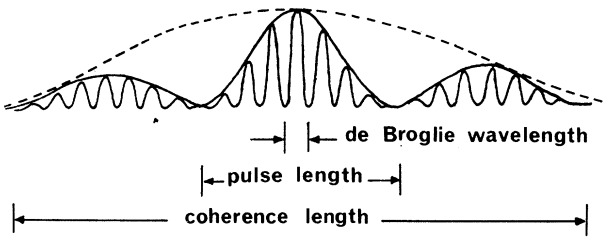


FIG. 1. Schematic diagram of the wave function relating the particle's deBroglie wavelength, the pulse length of the modulation, and the coherence length of the particle.

We now take the wave profile $F(t)$ to be a Guassian of width $2T$ which is modulated with fundamental frequency $\omega_0$,

$$F(t)=(2\pi T^2)^{-1/2}[\exp(-t^2/2T^2)]\times\sum_{n=-\infty}^{\infty}F_n\exp(-in\omega_0 t). \tag{6}$$

The parameter $T$ is characteristic of the coherence time, which is just the coherence length divided by the particle velocity. The quantity $\omega_0 T/(2\pi)$ measures the number of pulse lengths contained within the coherence length. It follows from Eqs. (5) and (6) that the Fourier transforms of $\vec{E}$ and $\vec{E}_p$ are simply related by

$$\vec{\mathcal{E}}(\vec{x},\omega)=\mathfrak{F}(\omega)\vec{\mathcal{E}}_p(\vec{x},\omega), \tag{7}$$

where

$$\mathfrak{F}(\omega)=\sum_{n=-\infty}^{\infty}F_n\exp[-\tfrac{1}{2}(\omega-n\omega_0)^2T^2]. \tag{8}$$

A similar expression holds for $\vec{\mathcal{B}}(\vec{x},\omega)$.

Equation (8), together with the condition that the integral of $F(t)$ be the charge, implies that in the small-$T$ limit (short coherence time) $\vec{\mathcal{E}}(\vec{x},\omega)\to\vec{\mathcal{E}}_p(\vec{x},\omega)$. However, in the large-$T$ limit, $\mathfrak{F}(\omega)$ becomes very sharply peaked at frequencies $n\omega_0$, and negligible elsewhere. Thus, the classical fields associated with the particle also get sharply peaked at these frequencies.

Our analysis has shown that the classical fields of an unmodulated wave train exist only for frequencies less than $T^{-1}$. From the known lifetimes of solid-state processes, one can estimate the coherence time for an electron emitted by a hot filament to be of the order of $10^{-9}$ to $10^{-10}$ sec. Thus, the fields associated with such

electrons ordinarily exist only up to microwave frequencies. However, Eq. (8) indicates that electrons modulated by a laser will give rise to fields at discrete frequencies far beyond $T^{-1}$. It seems plausible that the optical radiation observed by Schwarz and Hora[1] is due to the presence of these classical fields.

The justification of the use of the classical calculation at frequencies $\gg T^{-1}$ must await a full quantum mechanical treatment of the problem. Further investigation is needed to determine the details of the modulation process, the extent of the modulation, the details of the radiation mechanism, and the resulting intensities.

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## MANY-BODY PERTURBATION THEORY FOR MOLECULES BASED ON A UNITED ATOM MODEL*

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The linked-cluster many-body perturbation theory is developed for molecules using the united atom as a starting point. Specific application is made to hydrogen fluoride with neon as the united atom. The calculated energy for the molecule is found to be −100.4186 a.u. in excellent agreement with the experimental value of −100.4485 a.u. The theoretical correlation energy is found to be 92% of experiment. Satisfactory agreement is also obtained for the electric field at the fluorine nucleus.

The linked-cluster perturbation theory (LCPT)[1] has had remarkable success in the study of isolated[2,3] and interacting atoms.[4] In principle this procedure should be equally applicable to molecules.[5] The main difficulty in such an application is computational in nature, a consequence of multicenter feature of molecules. Recently[6] this procedure has been applied to study the energy and polarizability of the simplest neutral molecule, hydrogen. In order to gain a deeper insight into the role of various one-electron and multielectron processes influencing molecular properties, within the framework of the LCPT approach, it was felt necessary to investigate a complicated molecular system. The subject of study in the present work, namely, hydrogen fluoride (HF) provides a suitable system in this respect. It is large enough (10 electrons) to provide a detailed understanding of the many-body aspects of the problem, and yet simple enough so that the amount of computational effort is not prohibitive. In addition to our study of the energy of the HF molecule, we have subjected the calculated wave functions to a more severe test by examining the electric field at the fluorine nucleus. The latter analysis involves matrix elements closely analogous to those one needs for the evaluation of the variety of hyperfine properties. Information on such properties are currently available for HF and other molecules through microwave[7] and magnetic resonance, and molecular beam measurements.[8]

The choice of the HF molecule was dictated by some other considerations as well. Detailed variational Hartree-Fock[9] and configuration interaction (CI)[10] calculations have been performed on the HF molecule. These earlier investigations provide convenient references for comparison with our results. Also, in order to minimize difficulties connected with the two-center nature of the problem, we have used the united-atom Hamiltonian as the starting point for perturbation calculation. Intuitively, one expects the united-atom procedure to be reasonable for situations where a heavy atom is bonded to a relatively light one. HF is a typical example of such a system, and should be a good testing ground for this expectation. Information obtained with respect to this question is also of importance in deciding whether the united-atom procedure could be extended to the isoelectronic molecules $H_2O$, $NH_3$, and $CH_4$, which are of great chemical interest. For these molecules as well as HF, neon is the pertinent united atom.

The nonrelativistic Hamiltonian for HF (in atomic units) is given by

$$\mathcal{H}=\sum_{i=1}^{10}\left\{-\frac{1}{2}\nabla_i^2-\frac{9}{r_{\mathrm{F}i}}-\frac{1}{r_{\mathrm{H}i}}\right\}+\sum_{i>j}\frac{1}{r_{ij}}+\frac{9}{R_0}, \qquad (1)$$

where $r_{\mathrm{F}i}$ and $r_{\mathrm{H}i}$ are electronic coordinates measured with respect to F and H nuclei, respectively, and $R_0=1.7329$ a.u. is the internuclear sepa-