

far as the Fermi interactions for oxygen and nitrogen are concerned. The reasonableness of the approximations is indicated by the agreement of the nitrogen hfs in both molecules (see Table I). The values of the hfs coupling constants of the observable nuclear spin splittings in the organic radical are listed in Table II.

Using the results of YSHL we have calculated the O^{17} isotropic hfs in nitric oxide. It is given by the same mechanism involved in the nitrogen hfs; predominantly

TABLE I. Hyperfine structure for oxygen-17.

Molecule	O^{17} hfs $\times 10^{24}$ cm $^{-3}$		N^{14} hfs $\times 10^{24}$ cm $^{-3}$	
	exp.	calc.	exp.	calc.
$O^{16}O^{17}$	1.26	1.34, 1.17
$N^{14}O^{17}$...	0.63	0.85	0.71
$R_2N^{14}O^{17}$	0.617	...	0.79	...

from cross terms, in the configuration interaction wave function, between the ground state (2π) and various "excited" states having one (2π) and two (σ) unpaired electrons. The (σ) orbitals are composed of $1s$, $2s$, and $2p$ functions along the N-O bond. The agreement between the calculated splitting for O^{17} and that observed in the model compound is quite good. It is also interesting to compare these results with those found for molecular oxygen.^{1,6,7} In Table I the hfs due to O^{17} as well as that due to N^{14} are listed for the three examples. The electronic structure of molecular oxygen has been studied by Kotani, Mizuno, Kayama, and Ishiguro, who find $|\psi(0)|^2$ given predominantly by

TABLE II. Hyperfine structure constants in di-*sec*-butyl nitric oxide, $g=2.00585$, in benzene solution.

Nucleus	A (gauss)	$ \psi(r_N=0) ^2 \times 10^{24}$ cm $^{-3}$
N^{14}	13.39	0.79
H^1	3.84	0.0163
C^{13}	9.73	0.164
O^{17}	19.71	0.617

cross terms containing sigma orbitals from the ground (two unpaired spins) and "excited" (four unpaired spins, etc.) configurations.⁷ The value of the Fermi constant is about twice that observed in di-*sec*-butyl nitric oxide.

The experimental arrangement used in the present work consisted of a conventional 100-kc modulated EPR spectrometer operating at 9500 Mc/sec. A homogeneous 12-in. magnet was used. The time constant at the output of the 100-kc lock-in detector was 10 to 30 sec, when using a field sweep of 3 G/min. The linewidth is about 1 G. Magnetic-field measurements were made using a proton marginal oscillator whose frequency was

determined by a Hewlett-Packard 524C counter. The microwave frequency was determined using a Hewlett-Packard 540B transfer oscillator.

A more complete discussion of this particular organic radical and its relation to others in the series will be published in another paper.

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Extrema in Velocity Dependence of Total Elastic Cross Sections for Atomic Beam Scattering: Relation to Di-atom Bound States †

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UNDULATORY deviations from the Massey-Mohr (MM) dependence of the total elastic cross section $Q(v)$ for atom-atom scattering have been predicted¹ and observed.² The present communication indicates (1) a relationship between the maxima in $Q(v)$ and the number of stable di-atom bound states, and (2) a procedure for evaluating the potential from the extrema velocities. A single,³ static, central potential is assumed. The principles of the present treatment are general and are applicable to any "realistic" potential [long-range inverse power ($s \geq 3$) attraction, steep short-range repulsion]; for the purpose of concise illustration, however, the LJ (12-6) potential is employed here, using the notation of reference 1.

The extrema in $Q(v)$ are a consequence of the broad maximum in $\eta(l)$, which provides a significant number of nonrandom phases.¹ The maximum phase η^m increases with decreasing v and, assuming the attractive potential is sufficiently strong, can pass successively through $\pi/2$, π , etc., yielding substantial positive and negative deviations from Q_{MM} (calculated via the random-phase approximation).

We index the extrema in Q from high to low velocity, starting with $N=1$ for the first maximum, $N=1.5$ for the minimum which follows, etc., to $N=M$ for the maximum at lowest v . Analysis of the MM derivation reveals that the condition for greatest deviation from Q_{MM} is $\eta_N^m = \pi(N - \frac{1}{4})$. A semiclassical treatment⁴ shows that the maximum reduced phase depends solely upon $K \equiv \frac{1}{2}\mu v^2/\epsilon$, increasing monotonically with decreasing K . Also, l_m decreases toward zero as $k \equiv \mu v/\hbar$ decreases, so that $\eta^m(k)$ approaches $\eta_0(0)$. In the low-energy region the semiclassical approximation loses validity, and a partial wave analysis¹ is required. We note that, rigorously, $\eta^m(0) < \eta_0(0) + \pi/2$; in addition, considerations based on scattering-length theory

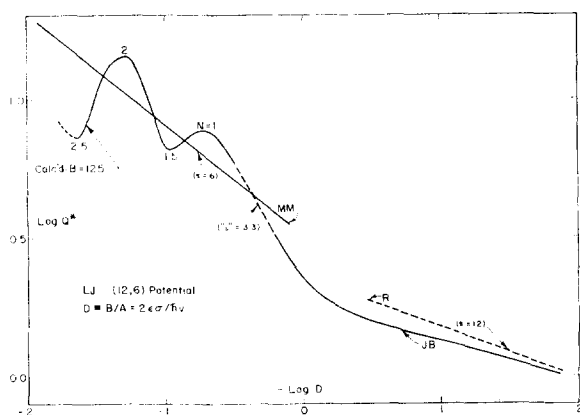


FIG. 1. Velocity dependence of the cross section.

strongly suggest⁵ that $\eta^m(k) < \eta^m(0)$. By Levinson's theorem⁶ $\eta_0(0) = n\pi$, where n is the number of discrete levels of zero angular momentum. Thus $N < n + \frac{3}{4}$, so that $M = n$; i.e., the number of maxima in $Q(v)$ equals the number of bound vibrational states of the di-atom.

Returning to the semiclassical analysis,⁴ we obtain for the LJ (12,6) potential $\eta^m = (120\pi/847) (231/160)^{1/6} D \cdot g(K)$, where $D \equiv B/A = 2\epsilon\sigma/\hbar v$ and $g(K) = 1 - 0.25K^{-4} + \dots \cong 1 - 0.25DB^{-4}$ (valid for $D \leq 2B^{1/4}$). With the previous formula for η_N^m this yields $N - \frac{1}{4} = 0.3012 (\epsilon\sigma/\hbar) v_N^{-1} [1 - 0.354(\epsilon/\mu)^{1/2} v_N^{-1}]$, where v_N is the velocity of the N th extremum. A plot of $N - \frac{1}{4}$ vs v_N^{-1} must pass through the origin; this serves to verify the assignment of the indices to the extrema. The initial slope of the line yields $\epsilon\sigma$; the curvature is governed by ϵ/μ . In addition, one may plot $(N - \frac{1}{4})v_N$ vs v_N^{-1} ; the ratio of slope to intercept yields separately ϵ , but with low sensitivity.

Consider next the "high-velocity" region (criterion: $\eta^m < \frac{1}{2}$). Using the Jeffreys-Born (JB) approximation for the LJ (12,6) phase¹ one obtains, upon rederiving the MM equation

$$Q_{JB}^* = \beta_1^2 \{ 2 + (1/10) (63\pi/128)^2 D^2 \beta_1^{-22} \times [1 - (640/147)\beta_1^6 + (2560/441)\beta_1^{12}] \}, \quad (1)$$

valid for $D \leq 1$, and usable as an approximation (within a few percent) to $D \cong 3$. Here β_1 is the root of $\beta^{11} +$

$(3\pi/4) D\beta^6 - (63\pi/128) D = 0$, where $\beta = (l + \frac{1}{2})/A$. As $D \rightarrow 0$, asymptotically $\beta_1 \sim 1.0404 D^{1/11}$ and $Q_R^* \sim (21/10) (63\pi/128)^{2/11} D^{2/11} = 2.273 D^{2/11}$, as expected for an inverse power ($s=12$) repulsive potential. This is to be compared with $Q_{MM}^* = 3.170 D^{2/5}$ ($s=6$ attraction only¹). Figure 1 shows a graph of Eq. (1), labeled JB; the straight lines R and MM designate Q_R^* and Q_{MM}^* . Shown also is an example of a curve of Q^* in the "low-velocity" region ($D \geq 3$), calculated¹ via the standard partial wave procedure, for $B=125$. The "wavelength" of the undulatory deviations decreases with increasing $\epsilon\sigma$, making resolution more difficult. Further discussion, including a consideration of the "amplitude" of the undulations (which decreases with increasing μ), is deferred to a detailed paper in preparation.

Applying the present procedures to the data of reference 2, one obtains for Li-Xe and K-Xe values for $10^{22}\epsilon\sigma$ (erg cm) of 9.4₅ and 6.7₂, respectively. Indexing of the extrema thus far observed² implies a minimum of three vibrational states each for the LiXe and KXe molecules in the $^2\Sigma^+$ state.

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Alternating Linewidths in the ESR Spectra of Dinitrobenzene Anion Radicals*

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WE have found an alternation in the linewidths in the ESR spectrum of the anion radical of *m*-dinitrobenzene. The radical was produced by electrolytic reduction in *N,N*-dimethyl-formamide solution at room temperature. The derivative spectrum obtained at -50°C shows that those hyperfine components corresponding to $m_N = \pm 1$ (where m_N is the total z component of the nitrogen nuclear spin angular momentum) are considerably broader and of smaller amplitude than those for which $m_N = \pm 2.0$. At room temperature, the effect is much weaker but may be detected by careful analysis of the spectrum. Examination of the spectra of the *p*- and *o*-dinitrobenzene