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PARTIAL AVERAGING IN CLASSICAL S-MATRIX THEORY; VIBRATIONAL EXCITATION OF H<sub>2</sub> BY He

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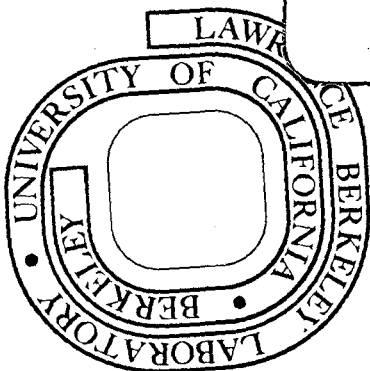
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PARTIAL AVERAGING IN CLASSICAL S-MATRIX THEORY;  
VIBRATIONAL EXCITATION OF H<sub>2</sub> BY He

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ABSTRACT

Within the framework of a general semiclassical theory that combines exact classical dynamics and quantum superposition it is shown how a certain averaging procedure allows one to treat some degrees of freedom in a strictly classical sense while others are quantized semiclassically. This enormously simplifies the application of the theory to three-dimensional collision systems and also leads to an interesting formal structure in the theory: the quantum-like degrees of freedom are quantized semiclassically via use of double-ended boundary conditions, while the unquantized classical-like degrees of freedom enter only through a phase space average over their initial coordinates and momenta. Preliminary results for vibrational excitation of  $H_2$  by He are presented and compared with available quantum mechanical calculations.

I. INTRODUCTION.

The last several years have seen an increasing use of classical trajectory calculations in describing inelastic and reactive molecular collisions<sup>1,2</sup>. The advantage of classical approaches is that the equations of motion can always be solved (at least numerically) without the necessity of introducing any dynamical approximations, whereas this is generally not the case for a quantum description. The shortcoming of a classical theory is, of course, that real molecules obey quantum rather than classical mechanics.

The object of our research in recent years has been to show how exact classical dynamics (i.e., numerically computed trajectories) can be used as input to a general semiclassical theory<sup>3,4</sup>. The principal physical idea is a natural extension of the Ford and Wheeler<sup>5</sup> treatment of potential scattering,

namely that one uses a quantum mechanical formulation of the scattering problem (so as to incorporate quantum superposition of probability amplitudes), but evaluates the dynamical parameters of the theory within the classical limit. For a collision between species which possess internal degrees of freedom the result of this semiclassical theory is a prescription for how one uses classical mechanics to construct the classical-limit of S-matrix elements, the "classical S-matrix", which are simply the probability amplitudes for transitions between specific quantum states of the collision partners. In a number of examples<sup>3</sup> it has been seen that this combination of "classical dynamics plus quantum superposition" accurately describes the quantum effects in molecular collisions.

One of the most practically important aspects of classical S-matrix theory is the ability to analytically continue classical mechanics in such a way as to describe classically forbidden processes, i.e., those which do not take place via ordinary classical dynamics; Section II discusses such processes in detail. This paper describes a feature of the theory that is particularly useful when some of the internal degrees of freedom are very classical-like, but others are highly quantized. This is common in an atom-diatom collision, for example, where there are typically a large number of rotational states that are strongly coupled and may thus be treated by strictly classical methods, but only a few vibrational states are involved so that this degree of freedom is highly quantum-like. The 'partial averaging' approach allows one to use a strictly classical Monte Carlo treatment of the classical-like degrees of freedom while the quantum-like degrees of freedom are quantized semiclassically - all without introducing any dynamical approximations into the theory. Preliminary results for vibrational excitation of  $H_2$  by He are presented in Section III.

## II. SUMMARY OF THE THEORY.

### A. Classically Allowed Transitions.

All formulæ in this paper will be written explicitly for non-reactive collisions of atom A and diatomic molecule BC. The cross section for collisional excitation of BC from initial vibration-rotation state  $(n_1, j_1)$  to final state  $(n_2, j_2)$ , summed and averaged over the m-components of the rotational states of BC, is given by

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^2 (2j_1 + 1)} \sum_J (2J + 1) \sum_{\ell_2, \ell_1} |S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J, E)|^2 \quad (2.1)$$

where  $S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J, E)$  is the S-matrix element for the A + BC collision system;  $E_1$  is the initial collision energy,  $k_1^2 = 2\mu E_1/\hbar^2$ ,  $E$  is the total energy,  $J$  is the total angular momentum, and  $\ell$  is the orbital angular momentum for relative motion of A and BC.

The classical limit of a particular S-matrix element is given by

$$S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J, E) = \left[ (2\pi)^3 \frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1} q_{j_1} q_{\ell_1})} \right]^{-1/2} \times \exp[i\phi(n_2 j_2 \ell_2, n_1 j_1 \ell_1)] \quad (2.2)$$

where  $\phi(n_2 j_2 \ell_2, n_1 j_1 \ell_1)$  is the classical action along the classical trajectory that is determined by the indicated double-ended boundary conditions (units are used such that  $\hbar = 1$ ); specifically,

$$\phi(n_2 j_2 \ell_2, n_1 j_1 \ell_1) = \int_{-\infty}^{\infty} dt \left[ -R(t) \frac{dP(t)}{dt} - q_n(t) \frac{dn(t)}{dt} - q_j(t) \frac{dj(t)}{dt} - q_\ell(t) \frac{d\ell(t)}{dt} \right] \quad (2.3)$$

where  $(R, P)$  are the translational coordinates and momenta for radial motion of

A and BC, and  $(q_n, n)$ ,  $(q_j, j)$ ,  $(q_\ell, \ell)$  are the action-angle variables for these degrees of freedom; the initial and final values,  $(n_1 j_1 \ell_1)$  and  $(n_2 j_2 \ell_2)$ , are required semiclassically to be integers. The pre-exponential factor in Equation (2) is the Jacobian relating the final values  $(n_2 j_2 \ell_2)$  to the conjugate initial values  $(q_{n_1}, q_{j_1}, q_{\ell_1})$  which lead to these specific final values; i.e., with  $(n_1 j_1 \ell_1)$  fixed, one varies  $(q_{n_1}, q_{j_1}, q_{\ell_1})$  to cause  $(n_2 j_2 \ell_2)$  to take on their desired final integer values.

Typically, however, there is more than one classical trajectory that satisfies these double-ended boundary conditions; Equation (2) is then a sum of similar terms, one for each such trajectory. In forming the square modulus of the S-matrix element as it appears in Equation (1) interference terms thus result. In the co-linear A + BC collision these interference effects are quite prominent (and are accurately described by classical S-matrix theory), but it has been noted that the sums that occur in Equation (1) diminish their effect for a three dimensional A + BC system; i.e., the interference terms are quenched.

If the interference terms are neglected, then it is easy to see that Equations (1) and (2) give

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}^{(E_1)} = \frac{\pi}{k_1^2 (2j_1 + 1)} \int dJ (2J + 1) \int d\ell_2 \int d\ell_1 (2\pi)^{-3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1} q_{j_1} q_{\ell_1})} \right|^{-1} \quad (2.4)$$

where it is assumed that enough integer values of  $J$ ,  $\ell_1$ , and  $\ell_2$  contribute to justify replacing the sums over them by integrals. If many integer values of  $n_2$  and  $j_2$  are accessible from the initial state  $n_1 j_1$ , then it is also convenient to average Equation (4) over a quantum number increment about  $n_2$  and  $j_2$ :



$$\sigma_{n_2 j_2 + n_1 j_1} \approx \frac{\pi}{k_1^2 (2j_1 + 1)} \int_0^\infty dJ (2J + 1) \int d\ell_1 \int d\ell_2 \int dn_2 \int dj_2$$

$$\times (2\pi)^{-3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1} q_{j_1} q_{\ell_1})} \right|^{-1}, \quad (2.5)$$

where the limits of the  $j_2$  and  $n_2$  integral are the integers plus and minus 1/2. In Equation (5) one can now change integration variables from  $(n_2 j_2 \ell_2)$  to  $(q_{n_1} q_{j_1} q_{\ell_1})$ ; this eliminates the Jacobian from the integrand, giving

$$\sigma_{n_2 j_2 + n_1 j_1} = \frac{\pi}{k_1^2 (2j_1 + 1)} \int_0^\infty dJ (2J + 1) \frac{\int^{j_1} d\ell_1}{|J - j_1|} \int d(q_{n_1}/2\pi) \int d(q_{j_1}/2\pi)$$

$$\int d(q_{\ell_1}/2\pi) \quad (2.6)$$

where the limits of the integral over  $q_{n_1}$ ,  $q_{j_1}$ , and  $q_{\ell_1}$  are values such that the final values of  $n$  and  $j$  are in the increment  $(n_2 + 1/2, n_2 - 1/2)$  and  $(j_2 + 1/2, j_2 - 1/2)$ , respectively.

The simplest way to evaluate Equation (2.6) is to sweep  $q_{n_1}$ ,  $q_{j_1}$ , and  $q_{\ell_1}$  through their complete domains  $(0, 2\pi)$ , putting the outcome of each trajectory into a quantum number 'box' labeled by the closest integer value of the final values of  $n$  and  $j$ ; this is essentially what is done in a standard Monte-Carlo calculation for this type of quantity. If interference effects are neglected, therefore, classical S-matrix theory for classically allowed processes reduces to standard Monte-Carlo methods.

As an aside regarding the above strictly classical expression, it is actually more consistent if one also averages the cross section over a quantum number width of the initial quantum numbers  $n_1$  and  $j_1$ ; this gives

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1} = \frac{\pi}{k_1^2 (2j_1 + 1)} \int dJ (2J + 1) \int d\ell_1 \int d(q_{\ell_1} / 2\pi) \int dj_1 \int d(q_{j_1} / 2\pi) \\ \times \int dn_1 \int d(q_{n_1} / 2\pi) \quad (1) \quad ,$$

the form of a complete phase space average over initial conditions; the limits of the  $n_1$  and  $j_1$  integrals are the initial integer values plus and minus 1/2. This latter expression, which treats initial and final states on an equal footing, satisfies microscopic reversibility.

#### B. Classically Forbidden Transitions.

In some cases there may be no classical trajectories (at the given energy) that connect the specific initial and final states  $(n_1 j_1)$  and  $(n_2 j_2)$ ; the transition is then said to be classically forbidden which in practice simply means that the process is 'weak', i.e., has a small transition probability. Vibrationally inelastic transitions in low energy collisions of light diatomics with atoms are usually such processes. Other important examples of classically forbidden processes are tunneling in reactive systems that have activation barriers and electronic transitions between different adiabatic electronic states.

Although there are no ordinary classical trajectories that contribute to these processes, it is in general possible to analytically continue classical mechanics and find complex-valued trajectories that do so. This can actually be accomplished by integrating the equations of motion with complex initial conditions and with a complex time variable. Along such complex-valued trajectories

the action integral  $\phi$  is complex, so that the S-matrix element in Equation (2.2) has an exponential damping factor,  $\exp(-\text{Im}\phi)$ ; classically forbidden processes are thus a generalization of the concept of tunneling in one-dimensional systems.

Just as for classically allowed processes, there may be several different classical trajectories (complex-valued ones) that contribute to the specific

S-matrix element in Equation (2.2); because of the sums that appear in Equation (2.1), however, it is still reasonable in most cases to disregard interference between these different trajectories. Furthermore, even though the  $n_1 j_1 \rightarrow n_2 j_2$  transitions is classically forbidden for  $n_1 \neq n_2$ , it will typically be true that many different  $j_2$  values have comparable probability. In such cases it is thus possible to average over a quantum number width of  $j_2$  as in Section IIA (replacing sums by integrals) but not for  $n_2$ .

Changing from integration over final values to integration over initial values as in Section IIA, thus gives

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^2 (2j_1 + 1)} \int_0^\infty dJ (2J + 1) \int_{|J - j_1|}^{J + j_1} d\ell_1 \int d(q_{j_1} / 2\pi) \int d(q_{\ell_1} / 2\pi) \times P_{n_2 \leftarrow n_1}(q_{j_1}, q_{\ell_1}, j_1, \ell_1; JE) \quad (2.7)$$

where

$$P_{n_2 \leftarrow n_1}(q_{j_1}, q_{\ell_1}, j_1, \ell_1; JE) \equiv 2\pi \left| \frac{\partial n_2}{\partial q_{n_1}} \right|^{-1} \exp[-2\text{Im}\phi] \quad (2.8)$$

$P_{n_2 \leftarrow n_1}$  is essentially a one dimensional-like vibrational transition probability that depends parametrically on the initial conditions of the other degrees of freedom and is calculated by holding the initial conditions  $(\ell_1, j_1, q_{\ell_1}, q_{j_1})$  constant while  $q_{n_1}$  is varied to make  $n_2$  equal to the desired integer value. The important practical advantage in this 'partial averaging' scheme is that one must deal with double-ended boundary conditions (through a root search procedure) only for the vibrational degree of freedom, the one that is being quantized semiclassically, with the orbital and rotational degrees of freedom

entering only through a phase space average over their initial conditions.

The four dimensional integral in Equation (2.7) can now be evaluated by Monte Carlo methods. Furthermore, one can obtain all partial cross sections - i.e., the distribution in final rotational quantum number  $j_2$  and/or the distribution in scattering angle (the differential cross section) - in the usual Monte Carlo fashion by assigning the numerical value of the integrand in Equation (2.7) to the appropriate 'box' labeled by  $j_2$  and scattering angle.

In summary, the only approximations involved in Equations (2.7) and (2.8) beyond classical S-matrix theory itself are (1) neglect of interference between different trajectories that lead to the same final values of  $l_2$  and  $j_2$ , and (2) replacement of sums over integer values of  $l_2$  and  $j_2$  by integrals. As has been noted, the interference terms would essentially average to zero even if they were included, and one only needs a few integer values of  $l_2$  and  $j_2$  to justify replacing the sums by integrals. The important practical advantage of this partial averaging approach is that double-ended boundary conditions (and the related root search) are required only for the quantized degrees of freedom (i.e., vibration), while the other (unquantized) degrees of freedom enter only through a phase space average over their initial conditions.

### III. RESULTS FOR He + H<sub>2</sub> COLLISIONS.

Calculations based on Equations (2.7) and (2.8) are being carried out for the He + H<sub>2</sub> collision system and its isotopic variants. The interaction potential is that of Gordon and Secrest<sup>6</sup>, and the H<sub>2</sub> potential is the accurate fit of Waech and Bernstein<sup>7</sup> to the Kolos-Wolniewicz potential.

Figure 1 shows our preliminary results for the total 0 → 1 vibrationally inelastic cross section as a function of the initial collision energy; i.e., the quantity shown is

$$\sigma_{1 \leftarrow 00}(E_1) = \sum_{j_2} \sigma_{1j_2 \leftarrow 00}(E_1) \quad (3.1)$$

Although these results are not final, they should be the correct semiclassical values to within at least a factor of 2. At 5 eV collision energy the  $0 \rightarrow 1$  transition is still classically forbidden; i.e., with  $E_1 = 5$  eV,  $n_1 = j_1 = 0$ , there are no values of  $J$ ,  $l_1$ ,  $q_{l_1}$ ,  $q_{j_1}$  for which a real-valued classical trajectory leads to  $n_2 = 1$ .

Fremerey and Toennies<sup>8</sup> have recently carried out coupled channel (i.e., quantum mechanical) calculations for this system and find a value of  $\sim 1.0 \times 10^{-4} \text{ \AA}^2$  for the total  $0 \rightarrow 1$  cross section at  $E_0 = 1.09$  eV. Within the uncertainty in our preliminary semiclassical results, therefore, there is excellent agreement with this quantum mechanical value.

Figure 2 shows the quantity  $\sigma_{1j_2 \leftarrow 00}$  as a function of  $j_2$  at  $E_0 = 3$  eV collision energy; i.e., this is the distribution in final rotational state that accompanies vibrational excitation from the ground state. Although  $j_2 = 0$  is the single most probable final rotational state, there is a significant amount of rotational excitation which accompanies the  $0 \rightarrow 1$  vibrational excitation.

Further calculations for this system are in progress and more details of the calculational procedure will be presented in a later report.

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FIGURE CAPTIONS

1. The cross section for excitation of  $H_2$  (by collision with He) from its ground state ( $n_1 = j_1 = 0$ ) to its first excited vibrational state ( $n_2 = 1$ ), summed over all final rotational states, as a function of initial collision energy; the quantity shown is defined by Equations (3.1) and (2.1). The arrow indicates the energetic threshold for this transition.
2. The distribution in final rotational states  $j_2$  that accompany the  $0 \rightarrow 1$  vibrational excitation in He +  $H_2$  collisions,  $\sigma_{1j_2} + 00$ , as defined by Equation (2.1). The initial collision energy is 3 eV.



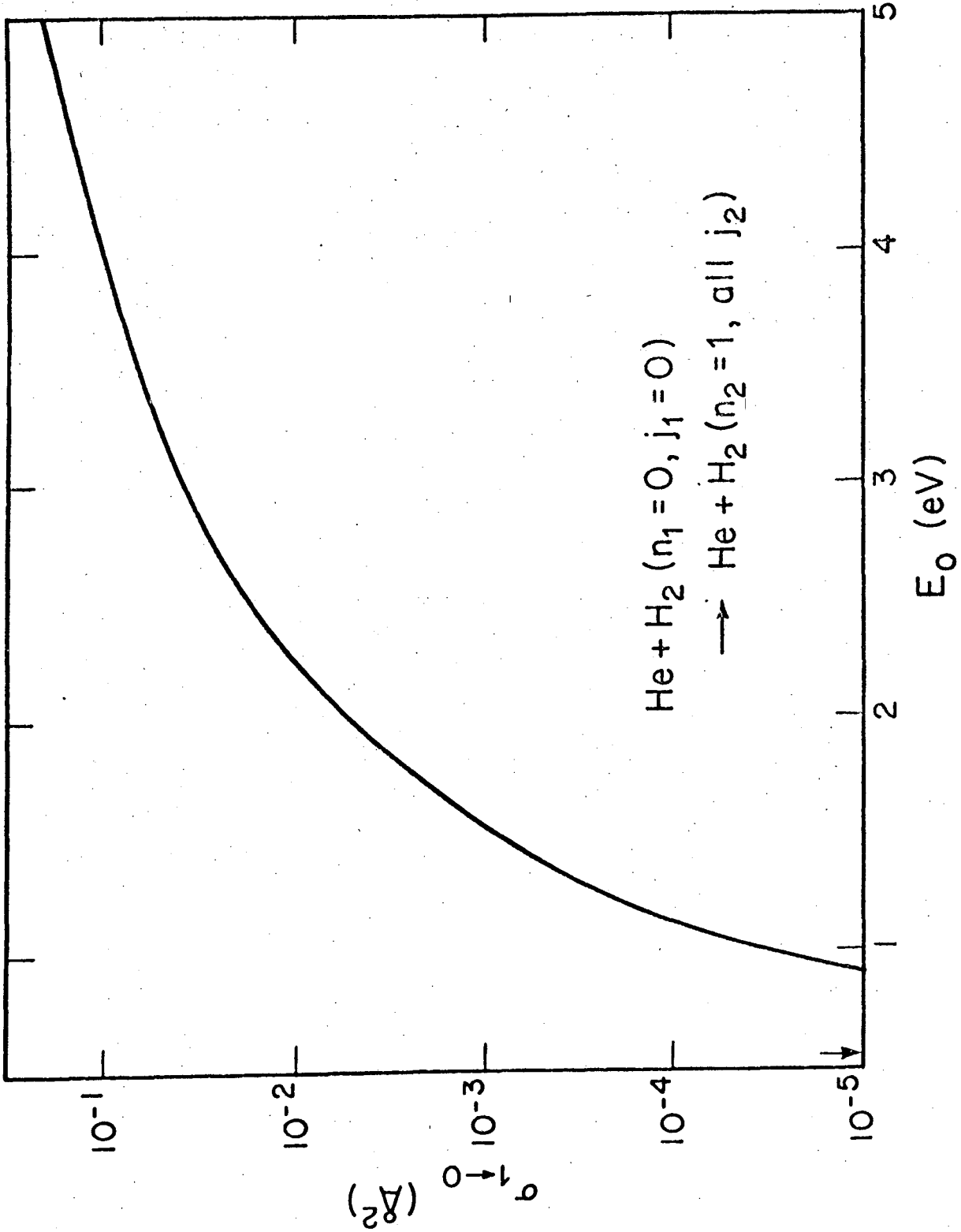


FIG. 1

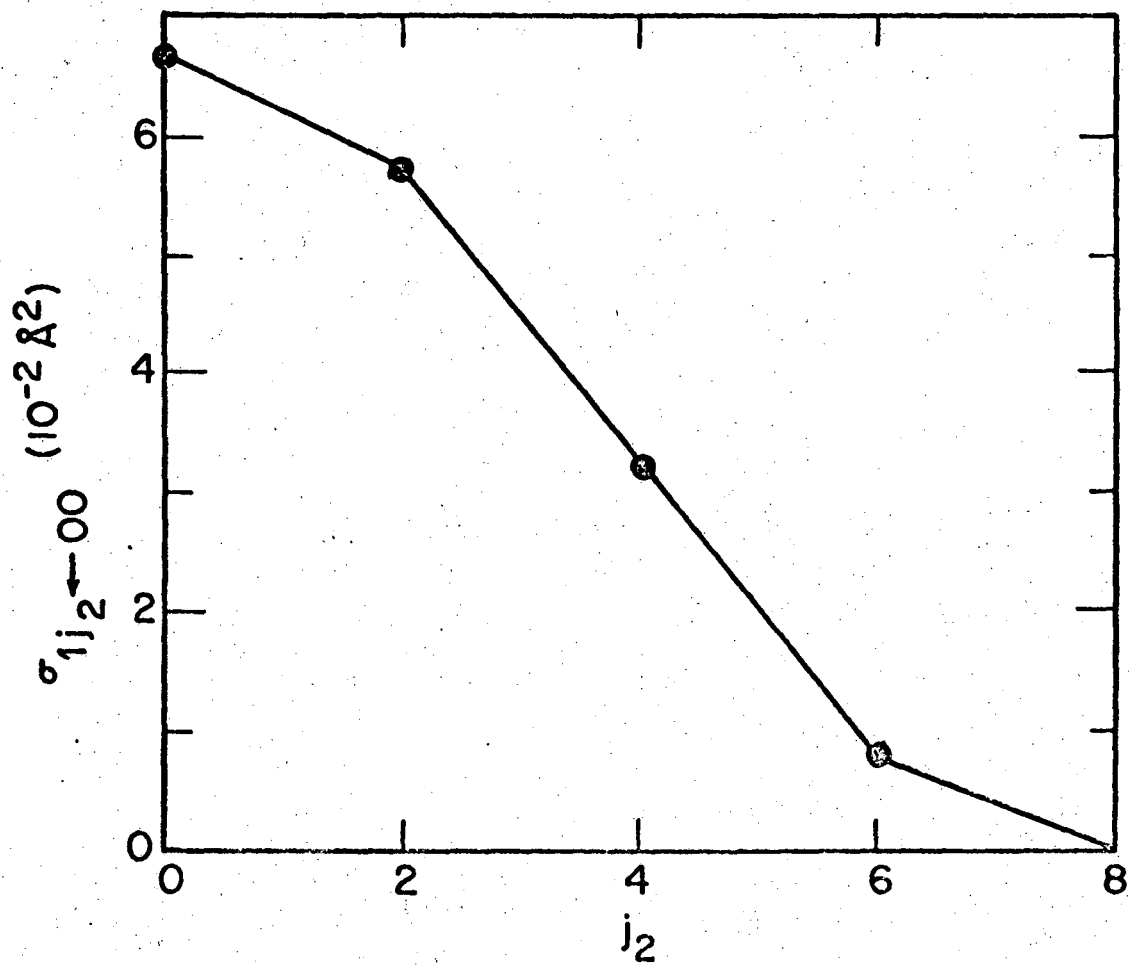


Fig. 2

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