

H_2^+ in Superintense Laser Fields: Alignment and Spectral Restructuring

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In superintense, relatively high-frequency fields, H_2^+ presents a strikingly different behavior from that found at lower frequencies. By applying the high-frequency Floquet theory of laser-atom interactions, we predict for the ground state progressive alignment of the molecular axis with the direction of a linearly polarized field as the intensity increases and persistence of the bond strength. The energy spectrum undergoes complete restructuring: while the field-free rotational levels become librational, they are gradually promoted with respect to the vibrational ones.

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The behavior of simple molecules in intense laser fields is now under active scrutiny. Much of the attention has focused on H_2^+ as the prototype of a molecular system. New phenomena have been detected, such as above-threshold ionization (ATI), above-threshold dissociation (ATD), bond-softening, and bond-hardening (trapping of vibrational population) [1], all of which have been anticipated theoretically [2].

In this paper, we explore the interaction of H_2^+ with superintense fields (of the order of 1 a.u. of intensity, 3.51×10^{16} W/cm²) at laser frequencies higher than the internal frequencies of the molecule in the field. This regime reveals an entirely different physical behavior of H_2^+ from the one studied so far at lower frequencies [1,2]. The method we use is stationary, high-frequency Floquet theory (HFFT) of laser-atom interactions, originally developed for atoms [3] and now extended to molecules [4]. In the atomic case, HFFT has been able to predict exotic phenomena such as stabilization [5], which has been recently observed experimentally [6].

We describe the radiation field in the dipole approximation and consider the case of *linear polarization* $\mathbf{A}(t) = -\alpha\hat{\mathbf{e}}\sin\omega t$, where $\hat{\mathbf{e}}$ is the unit vector in the direction of the field. The HFFT for H_2^+ proceeds from the space-translated Schrödinger equation for the relative motion [4,7]:

$$\left[\frac{\mathbf{\Pi}^2}{M} + \frac{\mathbf{P}^2}{2\mu} + \frac{1}{R} - \frac{1}{\left| \mathbf{r} - \frac{\mathbf{R}}{2} + \alpha(t) \right|} - \frac{1}{\left| \mathbf{r} + \frac{\mathbf{R}}{2} + \alpha(t) \right|} \right] \Psi(\mathbf{R}, \mathbf{r}) = i \frac{\partial \Psi(\mathbf{R}, \mathbf{r})}{\partial t}. \quad (1)$$

Here \mathbf{r} and \mathbf{R} are the relative electronic and nuclear coordinates, \mathbf{P} and $\mathbf{\Pi}$ are the relative electronic and nuclear momenta, and $\frac{1}{\mu} = \frac{1}{m} + \frac{1}{2M}$, where m and M are the electron and proton masses. The field is contained

only in $\alpha = \tilde{\alpha}_0 \hat{\mathbf{e}} \cos \omega t$, where $\tilde{\alpha}_0 = \alpha_0(1 + \frac{m}{M})$ and $\alpha_0 = I^{1/2} \omega^{-2}$.

By seeking stationary solutions of the Floquet type, Eq. (1) can be transformed into a system of coupled equations for the Floquet components of Ψ . At frequencies sufficiently high with respect to an average molecular excitation frequency in the field, this system reduces approximately to a single equation, which yields the structure of the molecule:

$$\left[\frac{\mathbf{\Pi}^2}{M} + \frac{\mathbf{P}^2}{2\mu} + \frac{1}{R} + V_0(\tilde{\alpha}_0; \mathbf{r} - \frac{\mathbf{R}}{2}) + V_0(\tilde{\alpha}_0; \mathbf{r} + \frac{\mathbf{R}}{2}) \right] u(\mathbf{R}, \mathbf{r}) = Eu(\mathbf{R}, \mathbf{r}). \quad (2)$$

The connection between the exact Ψ and u is $\Psi \approx u \exp(-iEt)$. The terms $V_0(\tilde{\alpha}_0; \mathbf{r} \pm \frac{\mathbf{R}}{2})$ entering Eq. (2) are the time averages of the corresponding ones in Eq. (1); they can be viewed as the electrostatic potentials generated by two "lines of charge" of length $2\tilde{\alpha}_0$, parallel to $\hat{\mathbf{e}}$ and centered on the protons at $\pm \mathbf{R}/2$, with higher charge density towards the end points (see Fig. 1). For a discussion of $V_0(\alpha_0; \mathbf{r})$ and for its analytic form, see Ref. [3].

The multiphoton ionization and dissociation rates of the HFFT are derived from transition amplitude formulas containing as initial and final states, bound and continuum solutions of Eq. (2). The rates vanish in the limit of large ω at fixed $\tilde{\alpha}_0$, i.e., the molecule is frozen to decay despite being strongly distorted (see Ref. [4]). The calculation of the rates at finite ω will be carried out in a subsequent stage.

As Eq. (2) is invariant only for rotations around the field axis $\hat{\mathbf{e}}$, and (separately) for reflections of the electronic and nuclear coordinates through the origin, the quantum numbers characterizing the manifolds of the solutions are M (total magnetic), P_e (electronic parity), and P_n (nuclear parity) [8].

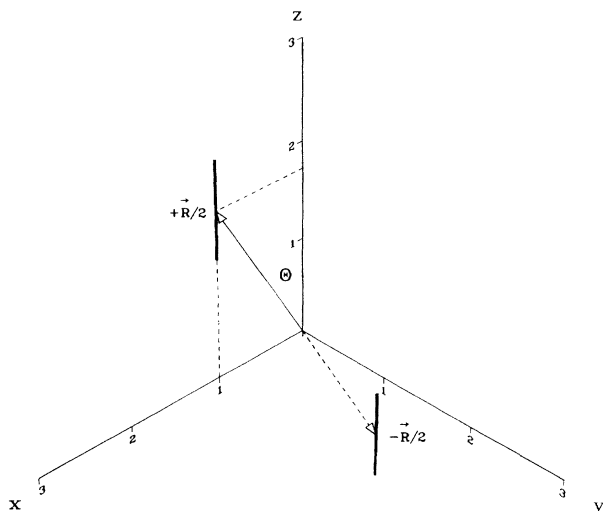


FIG. 1. "Lines of charge" generating the effective potential acting on the electron in Eqs. (2) and (3). These line segments of length $2\alpha_0$ are parallel to the field (taken along the z axis) and centered at the protons $\pm\mathbf{R}/2$; \mathbf{R} is the internuclear separation vector and we have taken $\Phi = 0$.

For solving Eq. (2), we adopt the Born-Oppenheimer (BO) approach, which in general is an excellent approximation (see Ref. [9]), because of the rapid character of the electronic motion. The first step is to solve for the *electronic motion in the field* with clamped nuclei:

$$\left[\frac{\mathbf{P}^2}{2} + V_0(\alpha_0; \mathbf{r} - \frac{\mathbf{R}}{2}) + V_0(\alpha_0; \mathbf{r} + \frac{\mathbf{R}}{2}) \right] \Phi_\gamma(\mathbf{r}; \mathbf{R}) = W_\gamma(\alpha_0; \mathbf{R}) \Phi_\gamma(\mathbf{r}; \mathbf{R}). \quad (3)$$

In order to be consistent with the BO approximation we are neglecting here and in the following all corrections of order $O(\frac{m}{M})$. When the direction of the internuclear axis \mathbf{R} is at an angle Θ with $\hat{\mathbf{e}}$, the total potential in Eq. (3) does not even have axial symmetry (see Fig. 1), and we are dealing with a three-dimensional (3D) nonseparable problem. The eigenvalues $W_\gamma(\alpha_0; \mathbf{R})$ will depend not only on the magnitude of \mathbf{R} but also on Θ . However, as easily shown, they do not depend on the azimuthal angle of \mathbf{R} around $\hat{\mathbf{e}}$.

In order to determine the nuclear motion, we make the BO ansatz in Eq. (2):

$$u_{\gamma n}(\mathbf{R}, \mathbf{r}) \approx \xi_{\gamma n}(\mathbf{R}) \Phi_\gamma(\mathbf{r}; \mathbf{R}), \quad (4)$$

to find

$$\left[\frac{\mathbf{\Pi}^2}{M} + \frac{1}{R} + W_\gamma(\alpha_0; \mathbf{R}) \right] \xi_{\gamma n}(\mathbf{R}) = E_{\gamma n} \xi_{\gamma n}(\mathbf{R}). \quad (5)$$

This equation gives the energy levels and eigenstates of the molecule at high frequencies and arbitrary intensity. Because of the axial symmetry, its solution is a two-dimensional (2D) nonseparable problem.

The eigenvalues of the electronic and nuclear equations were computed with the finite element method,

as described elsewhere [10]. In the 3D electronic code $W_\gamma(\alpha_0; \mathbf{R})$ was computed to an absolute accuracy of 10^{-4} . In the 2D nuclear calculation the accuracy of the levels $E_{\gamma n}$ is limited by that on $W_\gamma(\alpha_0; \mathbf{R})$, although the relative spacing $E_{\gamma n} - E_{\gamma n'}$ agrees with the most accurate field-free BO calculations [9] to better than 10^{-5} .

We have computed the *ground state* of the *electronic equation* (3), which in the field-free limit corresponds to the $1s\sigma_g$ state; the eigenvalue is denoted by $W_0(\alpha_0; \mathbf{R})$. We show in Fig. 2 the R and Θ dependence of the (axially symmetric) nuclear potential $U_0(\alpha_0; R, \Theta) = 1/R + W_0(\alpha_0; \mathbf{R})$ at various α_0 ranging from 0 to 2. At $\alpha_0 = 0$ we have the familiar angle-independent internuclear potential. For larger values of α_0 , two wells are formed, one around $\Theta = 0^\circ$ and the other around 180° (symmetric with respect to $\Theta = 90^\circ$), with a saddle at 90° . As a result, the nuclear potential $U_0(\alpha_0; R, \Theta)$ gives rise to a tangential force directed towards the field axis $\hat{\mathbf{e}}$, in addition to the usual radial force.

The *nuclear equation* (5) was solved with the nuclear potential $U_0(\alpha_0; R, \Theta)$ of the electronic ground state. At each α_0 , we calculated the lowest-lying

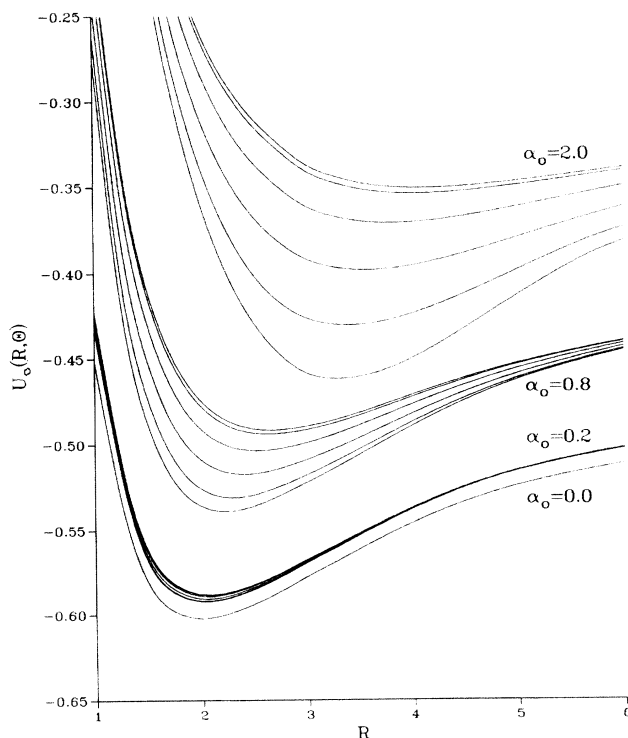


FIG. 2. Radial dependence of the lowest-lying potential surface $U_0(\alpha_0; R, \Theta)$ of H_2^+ in a linearly polarized radiation field (in a.u.), at various Θ , the angle between the direction of the molecular axis and the field. The lowest curve is the angle-independent field-free potential ($\alpha_0 = 0$). For the other values of α_0 , the six curves shown correspond successively to $\Theta = 0^\circ, 18^\circ, 36^\circ, 72^\circ, 90^\circ$, from bottom to top. $U_0(\alpha_0; R, \Theta)$ is symmetric in Θ with respect to 90° .

TABLE I. α_0 dependence of the lowest-lying energy levels E of the $M = 0$ manifold of H_2^+ in a linearly polarized field and of the dissociation energy D (in a.u.). E_H is the ground state energy of the H atom in the field. Each state is identified by its librational and vibrational nodal numbers, j and ν . When the gerade-ungerade levels have coalesced, only the gerade energy is given; the sign \sim means same energy as above.

$j \nu$	$\alpha_0 = 0$ E	$j \nu$	$\alpha_0 = 0.2$ E	$j \nu$	$\alpha_0 = 0.4$ E	$j \nu$	$\alpha_0 = 0.6$ E	$j \nu$	$\alpha_0 = 1.0$ E	$j \nu$	$\alpha_0 = 5.0$ E
0 0	-0.59712	0 0	-0.58595	0 0	-0.56616	0 0	-0.54586	0 0	-0.51109	0 0	-0.32426
1 0	-0.59686	1 0	\sim	1 0	\sim	1 0	\sim	1 0	\sim	1 0	\sim
2 0	-0.59633	2 0	-0.58366	2 0	-0.56112	2 0	-0.53858	0 1	-0.50168	0 1	-0.32040
3 0	-0.59554	3 0	-0.58344	3 0	\sim	3 0	\sim	1 1	\sim	1 1	\sim
4 0	-0.59449	4 0	-0.58243	4 0	-0.55697	0 1	-0.53648	2 0	-0.50000	0 2	-0.31658
5 0	-0.59321	5 0	-0.58122	5 0	\sim	1 1	\sim	3 0	\sim	1 2	\sim
6 0	-0.59168	6 0	-0.57987	0 1	-0.55672	4 0	-0.53239	0 2	-0.49294	0 3	-0.31279
7 0	-0.58993	7 0	-0.57812	1 1	\sim	5 0	\sim	1 2	\sim	1 3	\sim
8 0	-0.58796	8 0	-0.57635	6 0	-0.55395	2 1	-0.52963	2 1	-0.49142	2 0	-0.31122
0 1	-0.58716	0 1	-0.57621	7 0	-0.55356	3 1	\sim	3 1	\sim	3 0	\sim
1 1	-0.58691	1 1	\sim								
E_H	-0.5000		-0.4900		-0.4696		-0.4466		-0.4024		-0.2019
D	0.0971		0.0959		0.0966		0.0993		0.1087		0.1224

energy eigenstates of the $M = 0$ manifold, with both g_n and u_n parities. Results are given in Table I. The *ground state* experiences a substantial decrease in total binding energy $|E|$ with increasing α_0 , its value at $\alpha_0 = 5$ being reduced to about half that at $\alpha_0 = 0$. On the other hand, the dissociation energy of the molecule in the field, $D = |E| - |E_H|$, increases slightly over the interval (see Table I); here E_H is the hydrogen binding energy also *in the field*. This *persistence of bond strength* of the ground state at high relative frequencies is in sharp contrast to the bond softening manifested at lower frequencies [1,2]. Also striking is the behavior of the ground state eigenfunction represented in Fig. 3. The $\alpha_0 = 0$ case shows the familiar spherically symmetric ground state with quantum numbers $j = 0, \nu = 0$, concentrated radially around the equilibrium separation $R_e = 2.0$. However, already at $\alpha_0 = 0.2$ the situation has dramatically changed and the eigenfunction is split into two lobes, centered in the wells of $U_0(\alpha_0; R, \Theta)$ at $\Theta = 0^\circ$ and 180° . Thus the unrestricted rotational motion of the field-free H_2^+ reduces to a libration around the field axis. This *radiative alignment* effect is obviously due to the tangential force generated by the Θ dependence of the potential $U_0(\alpha_0; R, \Theta)$. At the same time, because of the splitting of the wave function into two nonoverlapping lobes, a nuclear gerade-ungerade degeneracy sets in, manifested in the coalescence of the lowest gerade and ungerade levels (see Table I).

The *excited states* can be characterized by the quantum numbers (j, ν) representing, respectively, the angular and radial nodes of the eigenfunctions. For field-free H_2^+ , (j, ν) are good quantum numbers. (The number of angular nodes in a plane passing through the polar axis is $2j$.) With the field on, this description, although approximate, holds to a very good extent [11]. The reason is that in the wells formed at $\Theta = 0^\circ$ and 180° , the internuclear po-

tential can be expressed approximately as $U_0(\alpha_0; R, \Theta) \approx f(\alpha_0; R) + g(\alpha_0; \Theta)/R^2$. This form of $U_0(\alpha_0; R, \Theta)$ allows *local separability* of the equation in these regions (the only ones of interest for the lower-lying states), and hence the introduction of j and ν , now representing the nodes of librational and vibrational motion in each well. (The number of angular nodes in a plane passing through the polar axis is again $2j$.) We have checked this assignment for all eigenfunctions calculated.

The binding energies of the nuclear excited states have the global tendency of decreasing with increasing α_0 , which is due to the fact that the potential $U_0(\alpha_0; R, \Theta)$ is shifted upwards for all values of R as α_0 increases. The excited state eigenfunctions show the same tendency of alignment as that of the ground state. The changes occurring in the potential $U_0(\alpha_0; R, \Theta)$ on the interval $0 < \alpha_0 < 5$ lead to a sweeping *restructuring of the energy spectrum*, apparent in Table I. On one hand, there is nuclear gerade-ungerade *coalescence* similar to that for the ground state, and, on the other, the *promotion* of the librational levels with respect to the vibrational ones.

Coalescent levels are those with quantum numbers (j, ν) and $(j + 1, \nu)$. By $\alpha_0 = 0.2$ only the pairs $(0,0),(1,0)$ and $(0,1),(1,1)$ have become degenerate. For $\alpha_0 \geq 0.6$, all such pairs shown in Table I are degenerate. Regarding the promotion mechanism, this is due to the fact that for increasing α_0 the two wells of $U_0(\alpha_0; R, \Theta)$ become progressively deeper with respect to Θ , but more extended radially (see Fig. 2). Hence the spacing of the coalesced librational levels increases, while that of the vibrational ones decreases, the consequence being that at $\alpha_0 = 5$ the lowest excited states are vibrational, the first librational pair coming only in fourth place. These changes obviously lead to a lot of (avoided) level crossings in the correlation diagram relating the $\alpha_0 = 0$ and large- α_0 limits [12].

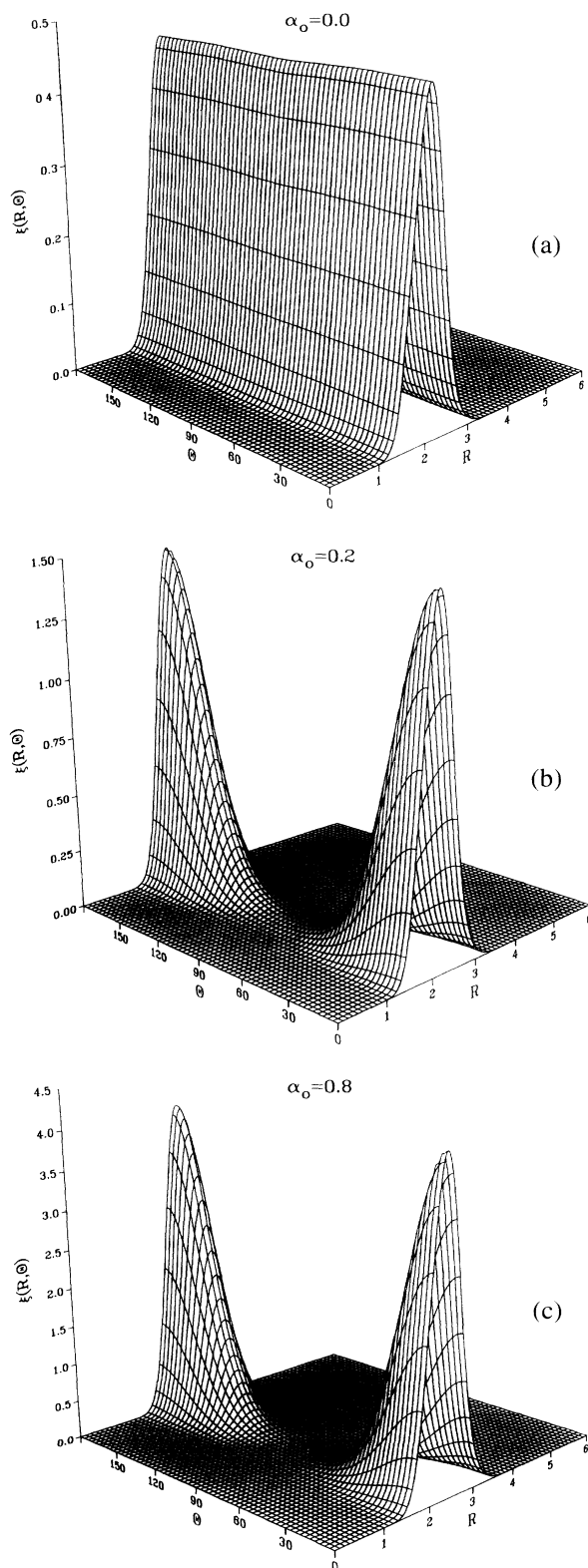


FIG. 3. Normalized Born-Oppenheimer nuclear ground state eigenfunction at $\alpha_0 = 0$, $\alpha_0 = 0.2$, and $\alpha_0 = 0.8$ as a function of R and Θ (in a.u.). Note the progressive radiative alignment for increasing α_0 .

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- [12] For a laser pulse [time dependent $\alpha_0(t)$], if certain conditions are met, the adiabatic time evolution of the molecular states will follow the energy curves of the correlation diagram, except at avoided crossings where diabatic transitions can occur; see Ref. [3], p. 444.

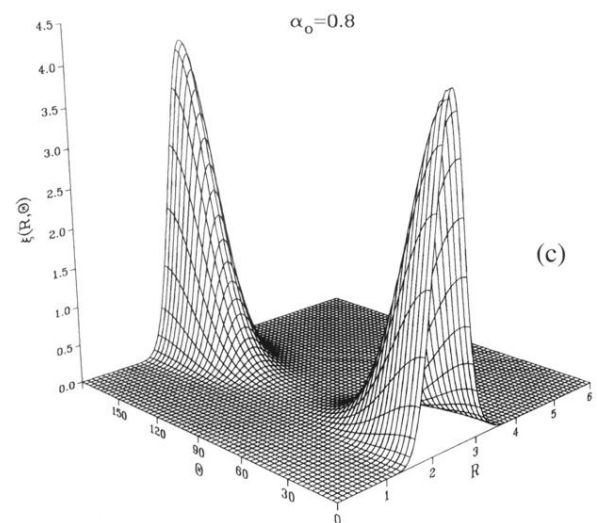
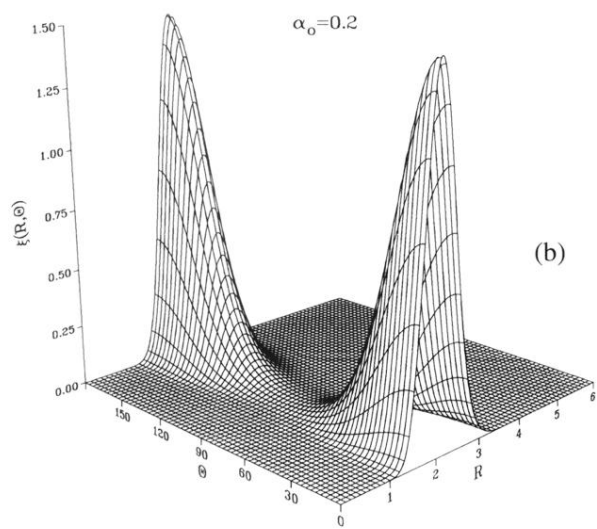
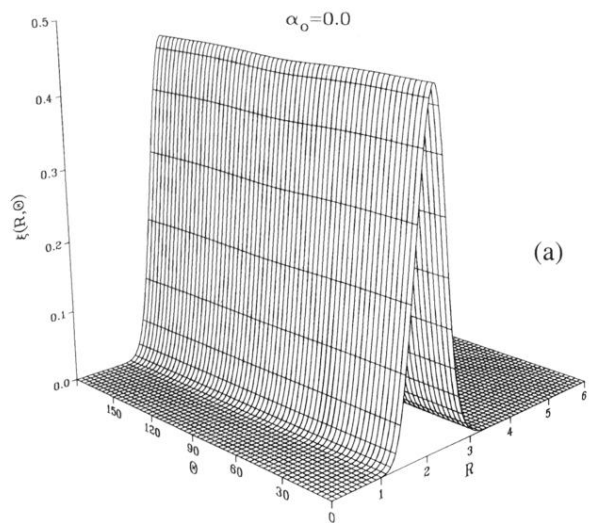


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