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# Adsorbed molecules in external fields: Effect of confining potential

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ABSTRACT

We study the rotational excitation of a molecule adsorbed on a surface. As is well known the interaction potential between the surface and the molecule can be modeled in number of ways, depending on the molecular structure and the geometry under which the molecule is being adsorbed by the surface. We explore the effect of change of confining potential on the excitation, which is largely controlled by the static electric fields and continuous wave laser fields. We focus on dipolar molecules and hence we restrict ourselves to the first order interaction in field-molecule interaction potential either through permanent dipole moment or/and the molecular polarizability parameter. It is shown that confining potential shapes, strength of the confinement, strongly affect the excitation. We compare our results for different confining potentials.



## 1. Introduction

Rotational excitation and hence the orientation and the alignment of the molecules in external fields has been a subject of great importance for the last few decades. The interest in manipulating the rotational motion has been a result of applications that molecular rotation plays in many branches of interdisciplinary nature [1]. Many new techniques have been proposed to orient/align the molecules theoretically [2–8] and many experiments also realized the orientation and alignment of molecules under different conditions [9,10]. Hence, controlling rotational motion of molecules has been an important aspect to explore other applications such as quantum computing [11] and information processing [12]. However, most of these studies were focused on freely rotating molecules. But, molecules confined under confinements behave differently as their rotational structure is different compared to free rotor. The confinement of molecules, corresponds to many practical situations [13,14] e.g. a molecule adsorbed on a surface is simple example of molecular confinement. Even in this case, different configurations lead to different confinements: vertically and horizontally adsorbed molecules. Another example of confined molecule is a molecule embedded in a crystalline solid, which is different from gas phase in the sense that internal fields come into picture. Due to these fields alignment in this case does not show revival structures [15]. Another class of confining potentials like $V_0\cos 2\vartheta$ and $V_0(1-\cos 2\vartheta)$, where $V_0$ is the confining potential and $\vartheta$ is the angle between molecular axis and normal to the surface, have been introduced by Curl et al. [16] and MacRury and Sams [17] to study adsorption of $H_2$ by zeolites. The study of hindered or confined rotor is applied in many situations such as the eigen energies of confined rotors are required for statistical reaction rate theories and for evaluation of the thermodynamic quantities of interest such as partition function, specific heat etc. [18].

Recently Alvarez-Castilla et al. have introduced cotangent ($cot\vartheta$) type of potential to study hindered rotations [19]. They have shown that with this hindering potential, the Schrödinger equation is exactly solvable. In some other cases, particularly in case of $H_2$ adsorbed on a surface, the potential governing the motion of the rigid rotor is given by

$$V(\tau, z) = V_0 + c\tau^2 + k(z - z_0). \quad (1)$$

$\tau = cos\vartheta$, $z_0$ is the equilibrium position normal to the surface, $\vartheta$ is the angle between molecular axis and the normal to the surface. $V_0$, $c$ and $k$ are constants. $c$ may be negative or positive 3. The molecule is supposed to be hindered along the surface, if c is positive. In the case of negative c value [20], the hindrance is perpendicular to the surface. In addition, there are few other potentials taken in the literature although not strictly for adsorbed molecules, but for different interdisciplinary applications [21]. In this work we investigate the excitation of rotational motion, orientation and alignment of a diatomic molecule, in order to

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understand the role of confining potentials. The Schrödinger equation for the confined rotor is solved by finite difference method [22]. It is shown that the different coupling elements between various rotational states vary along with confining potentials. As confining potential parameters such as confinement strength, confining angle etc. change, the rotational levels also change, leading to the changes in various coupling elements such as $<\psi(i)|cos\vartheta|\psi(j)>$, $<\psi(i)|cos^2\vartheta|\psi(j)>$ etc. These coupling elements are responsible for the response of such systems to external fields. The cases we consider here are finite confining potential, unlike previous studies on the subject where infinite square potential has been taken. As in case of infinite confining potential the analytical solution of the Schrödinger equation is possible, but in case of finite strength of the potential the numerical solutions is always preferred. Hence we solve the equation numerically and find the rotational states of the confined rotor and in addition the coupling elements are also calculated. We show the variation of energy levels, probabilities of

**Table 1**
Few coupling matrix elements, $<\chi_{j'm'}|\cos^n\vartheta|\chi_{jm}>$, in hindered rotor, for different confining potentials.

| $n$ | $j'm'-jm$ | Free rotor | $V_0$ | CASE-I | CASE-II | CASE-III | CASE-IV |
|---|---|---|---|---|---|---|---|
| 1 | 00–10 | $V_0=10$ | 0.5774475303 | 0.3854702173 | 0.3493822427 | 0.4028139082 | 0.2735590141 |
| 1 | | $V_0=20$ | | 0.1307447963 | 0.2025985806 | 0.3364755257 | 0.2599899821 |
| 1 | | $V_0=50$ | | 0.0314790209 | 0.1472097978 | 0.2663166485 | 0.2484212611 |
| 1 | 10–20 | $V_0=10$ | 0.5165691856 | 0.4567220832 | 0.4563914848 | 0.5422617335 | 0.0174756312 |
| 1 | | $V_0=20$ | | 0.4296670691 | 0.4451876187 | 0.4810324452 | 0.0174201962 |
| 1 | | $V_0=50$ | | 0.4669524298 | 0.5791328548 | 0.3780137432 | 0.0252317351 |
| 1 | 20–30 | $V_0=10$ | 0.5073442536 | 0.4826990146 | 0.5382856941 | 0.5501113397 | 0.0017908476 |
| 1 | | $V_0=20$ | | 0.4705541165 | 0.5502282736 | 0.5586418046 | 0.0014874829 |
| 1 | | $V_0=50$ | | 0.4933443425 | 0.4667860357 | 0.4678512096 | 0.0012279889 |
| 1 | 30–40 | $V_0=10$ | 0.5042856637 | 0.4946136990 | 0.5024122379 | 0.5268316245 | 0.0000175614 |
| 1 | | $V_0=20$ | | 0.4923859160 | 0.4999750245 | 0.5507104395 | 0.3647357607 |
| 1 | | $V_0=50$ | | 0.5079888161 | 0.5007984285 | 0.5435107111 | 0.0000007801 |
| 1 | 40–50 | $V_0=10$ | 0.5029335409 | 0.5017282344 | 0.5071831139 | 0.5162909036 | 0.0000436260 |
| 1 | | $V_0=20$ | | 0.5031423079 | 0.5161380537 | 0.5303446891 | 0.0000681378 |
| 1 | | $V_0=50$ | | 0.4981667488 | 0.5417640058 | 0.5692266274 | 0.0001088144 |
| 1 | 50–60 | $V_0=10$ | 0.5022414391 | 0.5027347652 | 0.5007665085 | 0.5112669261 | 0.4457163694 |
| 1 | | $V_0=20$ | | 0.5020372898 | 0.4955423019 | 0.5203203491 | 0.0000673990 |
| 1 | | $V_0=50$ | | 0.4858663242 | 0.4679755350 | 0.5511391981 | 0.0001088144 |
| 1 | 60–70 | $V_0=10$ | 0.5018581055 | 0.5002352135 | 0.4979942115 | 0.5084087450 | 0.4640605527 |
| 1 | | $V_0=20$ | | 0.4969652388 | 0.4946088483 | 0.5149037600 | 0.0000690092 |
| 1 | | $V_0=50$ | | 0.4826447190 | 0.4909269952 | 0.5352684447 | 0.0001108768 |
| 2 | 00–20 | $V_0=10$ | 0.2982147647 | 0.2494957163 | 0.2497470631 | 0.1947944085 | 0.2315463489 |
| 2 | | $V_0=20$ | | 0.1546278007 | 0.2111683555 | 0.1425590572 | 0.2351256389 |
| 2 | | $V_0=50$ | | 0.0790469558 | 0.1263492482 | 0.0935885185 | 0.2262895338 |
| 2 | 10–30 | $V_0=10$ | 0.2619630514 | 0.2257759318 | 0.2489076146 | 0.2607642902 | 0.1654382239 |
| 2 | | $V_0=20$ | | 0.1985203542 | 0.2508264001 | 0.2257936691 | 0.2038327580 |
| 2 | | $V_0=50$ | | 0.2272576028 | 0.2746037422 | 0.1530133608 | 0.2377433239 |
| 2 | 20–40 | $V_0=10$ | 0.2556878744 | 0.2445017456 | 0.2647418766 | 0.2577194454 | 0.1571118618 |
| 2 | | $V_0=20$ | | 0.2367143560 | 0.2694535645 | 0.2564712005 | 0.0022120850 |
| 2 | | $V_0=50$ | | 0.2538078333 | 0.2501081294 | 0.2044419527 | 0.2008359372 |
| 2 | 30–50 | $V_0=10$ | 0.2534197272 | 0.2510042161 | 0.2546202309 | 0.2531049713 | 0.0395265435 |
| 2 | | $V_0=20$ | | 0.2508802913 | 0.2561242125 | 0.2524943879 | 0.0006110152 |
| 2 | | $V_0=50$ | | 0.2572857524 | 0.2658344881 | 0.2414691772 | 0.2221843958 |
| 2 | 40–60 | $V_0=10$ | 0.2523475473 | 0.2530316292 | 0.2535038987 | 0.2522301357 | 0.0000187945 |
| 2 | | $V_0=20$ | | 0.2539685266 | 0.2545237671 | 0.2510444924 | 0.0492093491 |
| 2 | | $V_0=50$ | | 0.2487504360 | 0.2509576559 | 0.2484581193 | 0.1632912997 |
| 2 | 50–70 | $V_0=10$ | 0.2517633259 | 0.2521714530 | 0.2535038987 | 0.2517347332 | 0.1569248277 |
| 2 | | $V_0=20$ | | 0.2516378948 | 0.2491224666 | 0.2512070061 | 0.1200549543 |
| 2 | | $V_0=50$ | | 0.2420205652 | 0.2398572927 | 0.2469748984 | 0.1914222418 |
| 3 | 00–10 | $V_0=10$ | 0.3464662293 | 0.2805507619 | 0.2052695948 | 0.1731118277 | 0.2132342597 |
| 3 | | $V_0=20$ | | 0.1245026776 | 0.1252232851 | 0.1091293140 | 0.2162560542 |
| 3 | | $V_0=50$ | | 0.0507318603 | 0.1274892924 | 0.0549323599 | 0.2193249193 |
| 3 | 00–30 | $V_0=10$ | 0.1512309521 | 0.1580378153 | 0.1404860937 | 0.0805554251 | 0.1194835753 |
| 3 | | $V_0=20$ | | 0.1376904203 | 0.1169914026 | 0.0556133840 | 0.1175764071 |
| 3 | | $V_0=50$ | | 0.1045351805 | 0.0578153852 | 0.0335893941 | 0.0988289104 |
| 3 | 10–20 | $V_0=10$ | 0.4427717594 | 0.3689432382 | 0.3812737427 | 0.3921857654 | 0.0981528068 |
| 3 | | $V_0=20$ | | 0.3049033659 | 0.3526948168 | 0.2955737296 | 0.0985285587 |
| 3 | | $V_0=50$ | | 0.2881756999 | 0.3725953072 | 0.1555215907 | 0.1128720170 |
| 3 | 10–40 | $V_0=10$ | 0.1320191602 | 0.1197970733 | 0.1162584341 | 0.1041646540 | 0.0114217689 |
| 3 | | $V_0=20$ | | 0.1022668028 | 0.1146893479 | 0.0785482254 | 0.1168204642 |
| 3 | | $V_0=50$ | | 0.1178027598 | 0.1614219187 | 0.0518819825 | 0.0438723683 |
| 3 | 20–30 | $V_0=10$ | 0.3945967412 | 0.3548030555 | 0.4209916170 | 0.4558406288 | 0.0364226269 |
| 3 | | $V_0=20$ | | 0.3349268804 | 0.4359015051 | 0.4418439091 | 0.0335174332 |
| 3 | | $V_0=50$ | | 0.3642455976 | 0.4146447998 | 0.2851054535 | 0.0306723372 |
| 3 | 20–50 | $V_0=10$ | 0.1284860123 | 0.1275287099 | 0.1313996296 | 0.1114360379 | 0.0122220180 |
| 3 | | $V_0=20$ | | 0.1239273670 | 0.1337896311 | 0.0931294913 | 0.2231148550 |
| 3 | | $V_0=50$ | | 0.1301947530 | 0.1180087174 | 0.0592867539 | 0.0036009967 |
| 3 | 30–40 | $V_0=10$ | 0.3850846689 | 0.3677452474 | 0.3981363507 | 0.4270635908 | 0.0026185420 |
| 3 | | $V_0=20$ | | 0.3627863869 | 0.4049613354 | 0.4610393829 | 0.1951297545 |
| 3 | | $V_0=50$ | | 0.3870632328 | 0.4072535552 | 0.4170274314 | 0.0070780319 |