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Study of electronic structure and excitation function for [He, H_2^+(v, j=1)] system

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Abstract— ***The electronic structure of the title Vander Waals system and asymptotic behaviour of its diatomic potential energy (PE) function considered to be part of a 3D potential energy surface (PES) (MTJS) of the title system were re-investigated. The first and second derivatives of this PE were calculated. While plots of the different diatomic potentials match exactly in the range of interest, their derivatives differ leading to somewhat different classification of trajectories in their quasi-classical trajectory (QCT) treatment. Different dynamical features, like the excitation functions for exchange and dissociation reactions of the system, as obtained from the PES and another more accurate PES reported by Aquilanti et al. have been compared with one another and with the experiment.***

Keywords— ***PES, Translational Energy, Vibrational Energy, Excitation Function***

I. INTRODUCTION

Electronic structure and dynamical processes in the title system have been intensively studied over the past four decades experimentally as well as theoretically [1-20]. One of the methods used to study these dynamical processes is the QCT. Schreiber used a simple algorithm for the QCT method which employs WKB energies and in turn, the first and second derivatives of diatomic potential function to classify different trajectories [21].

Joseph and Sathyamurthy (JS) used an extended Rydberg function for the diatomic PE and Sorbie-Murrell function for triatomic PE to fit the energy data of McLaughlin and Thomson (MT) and obtained reaction cross sections (σ^R) using the QCT method [22,23]. Kumar and Sathyamurthy (KS) extended the application of this PES to study dissociation dynamics of HeH_2^+ [24]. Joseph and Sathyamurthy [22] found near-quantitative agreement between (3D QCT) theory and experiment for the vibrational enhancements of σ^R, dissociation cross section (σ^D) and branching ratio (Γ). Nevertheless, some quantitative discrepancies remained in respect of some of the experimental results [22, 23], notably

(i) at vibrational quantum number (v) = 0, QCT theory underestimates σ^R values at low energies,

(ii) QCT results agree with those of Turner et al. [17] in $\sigma(E_{tot})$ = constant at around E_{tot} = 5.0 eV, when CRB's σ^R starts decaying, (iii) for v = 1 to 4, the values of σ^R of CRB and Lee et al. agree only at high end of E_{tot}.

Three sources of discrepancies were pointed out:

(a) the QCT approach may not be rigorously valid,

(b) the fit of the *ab initio* PES might not be sufficiently accurate and

(c) the experiments might need refinement.

Experimentally, the endothermic ion-molecule reaction

$H_2^+ + He \rightarrow HeH^+ + H, \quad \Delta H = 0.806$ eV, (1),

and the competing endothermic collision induced dissociation (CID) process

$H_2^+ + He \rightarrow H^+ + H + He$, $\Delta H_{II} = 2.651$ eV, (2) were studied at low collision energies by CRB (Chupka, Berkowitz, and Russell [5-7]) despite the difficulties related to the positive charge of one of the reactants, using photo-ionization technique. They obtained scattering cross section σ^D (E_{trans}) for dissociative and σ^R (E_{trans}) for exchange reactions as functions of translational energy, E_{trans}, for v = 0 to 5. While the excitation function σ^R (E_{trans}) have a pronounced peak near threshold, the other excitation function, σ^D (E_{trans}) increased steadily from the dissociation threshold (E_{th}^{diss}); and channel (2) dominated over channel (1) at $E_{trans} >> E_{th}^{diss}$. It was also found that vibrational energy E_{vib} is much more effective than E_{trans} in promoting both the reactions (1) and (2).

Around 1987, Govers et al. (GG) experimentally investigated reactions (1) and (2), using the threshold–photoelectron / photo-ion coincidence (TPEPICO) technique [19]. They studied the vibrational-energy dependence of σ^R and σ^D for the reactions (1) and (2) at $E_{trans} = 3.1 \pm 0.7$ eV for v = 0 to 6, and reported vibrational enhancements of magnitude comparable with that of other experiments. They also found that the branching ratio Γ remains approximately constant, at about 0.3 for $v \leq 3$ and rises through 1.3 for higher v's. Both the reactions involve hard-type collisions resulting in large angle scattering for v .

Tang et al. [20] have measured translational energy dependence of cross sections (σ^R) using a pulsed-field ionization–photoelectron-secondary ion coincidence (PFI-PESICO) approach for higher vibrational levels at translational energies of 0.6 and 3.1 eV.

Theoretically, some improvements have been made in the meanwhile. An accurate PES has been proposed by Aquilanti et al. (AEA) [25], based on *ab initio* energy points calculated at MRCI level, using diatomic PE of Aguado and Paniagua [26], and a triatomic polynomial of 6th order. They also used a 12th order polynomial PES [27], but unfortunately, later reported it to be incorrect [28].

Using QCT program and this 12th order PES (polynomial) of Palmieri et al. [27] Tang et al. [20] calculated the proton transfer cross section (σ^R) as well as the cross section (σ^D) for reaction (2). Their experimental values of σ^R are higher than those of QCT at low collision energies. However, the inaccuracy of the fit might have rendered the PES not offer a reliable result. Also, the features like the sharp peaks for lower vibrational state and decay of the excitation functions could not be reproduced in the work of AEA [25] or Maiti et al. [29].

Therefore, in this paper our aim is to examine analytical properties of the 6th order PES of Aquilanti et al. and compare it with that of the MTJS surface as it relates to the classification of the trajectories, and to investigate the accuracy of the surfaces with respect to the excitation functions as compared to experiment.

II. METHODOLOGY

FORTRAN 77 codes were written for the 6th order polynomial PES of the titled system described by AEA [25]. From these codes the following values were obtained for the energies of the reactants, linear intermediate and products after adding energy of the dissociation state. They are -3.506053, -3.518587 and -3.478171 hartree which may be compared with the corresponding values of -3.505776, -3.518181 and -3.478190 hartree obtained by AEA themselves. The diatomic part of the potential was then calculated for H_2^+ and HeH^+. This was compared with that calculated from JS and MT data. All the three plots were found to match exactly from r_{AB} = 0 to 10 Å (not shown here).

The first and second derivatives of the diatomic potential functions for the potentials of AEA for H_2^+ and HeH^+ were also programmed in FORTRAN 77 (the derivatives for MTJS surface could be extracted from the trajectory program of JS [22]). Both the derivatives were plotted against diatomic distances, r_{AB} in eV/Å (electron volt per angstrom) and eV/Å^2 (electron volt per square angstrom), r_{AB} was varied from zero to 10 Å.

Dynamical attributes of both the exchange and CID reactions (1) and (2) were calculated using the QCT theory, the details of which are described in literature [30-33]. For our calculations, we used REACTS Program of Schreiber [34]. The diatomic vibrational energy levels were determined as discussed in Ref. [21]. The initial separation of the atom He from the diatom H_2^+ was set at 6.0 Å, where interaction energy was almost zero. The impact parameter b was chosen by stratified sampling at intervals of 0.5 Å, and 2000 trajectories were run per stratum. All other variables were selected randomly by the standard procedure [31-34].

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Hamilton's equations were solved numerically using the fifth-order predictor-sixth order corrector Adams-Moulton method. The accuracy of the integration was checked from conservation of energy and angular momentum. Energy conservation was better than 10^{-5} eV.

A. Figures and Tables

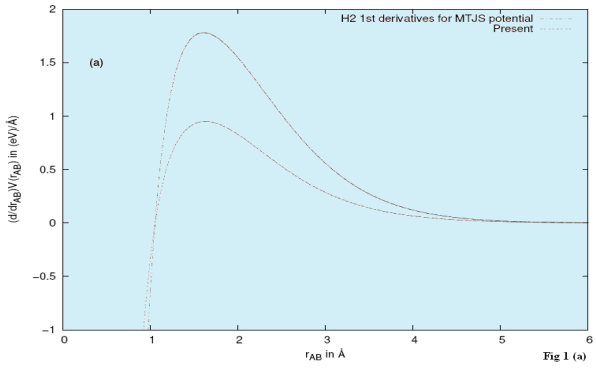

Fig 1 (a)

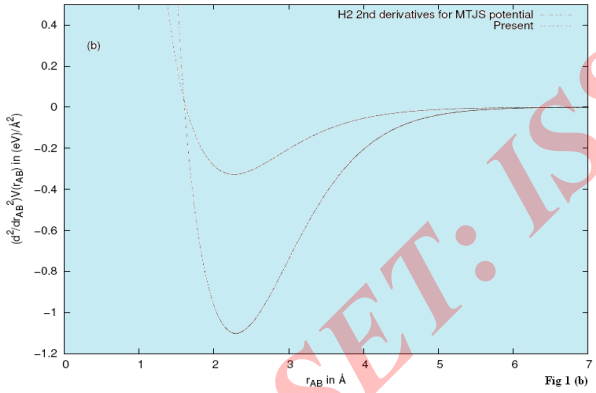

Fig 1 (b)

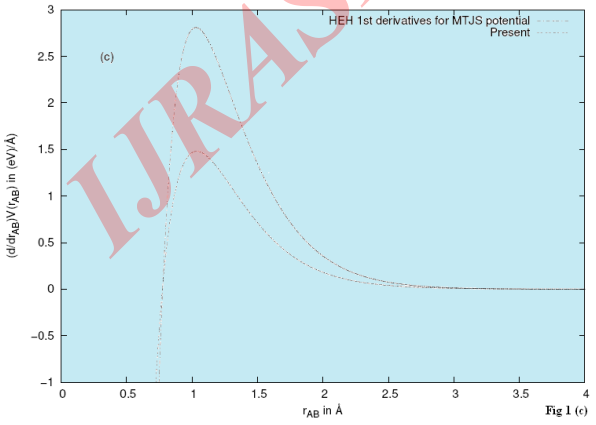

Fig 1 (c)

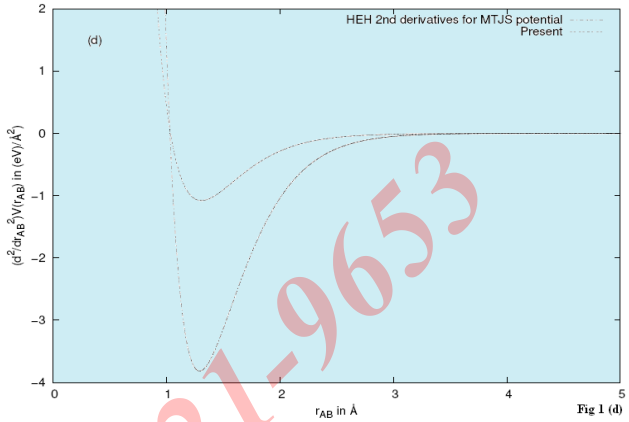

Fig 1 (d)

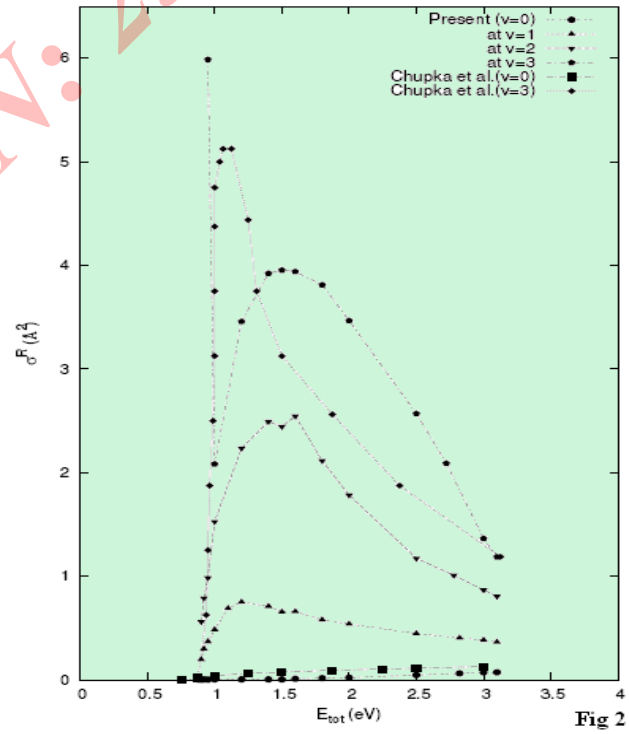

Fig 2

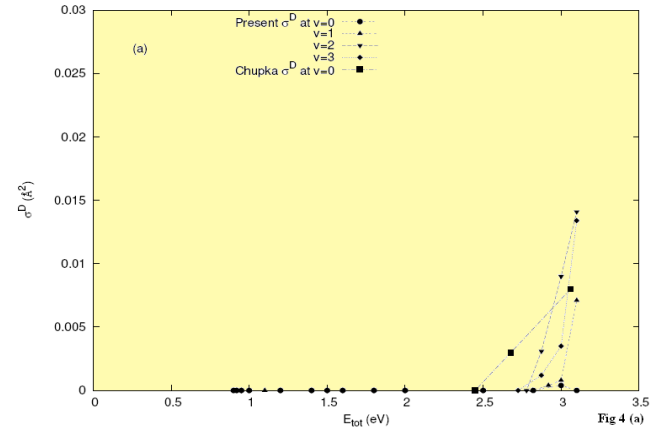

Fig 4 (a)

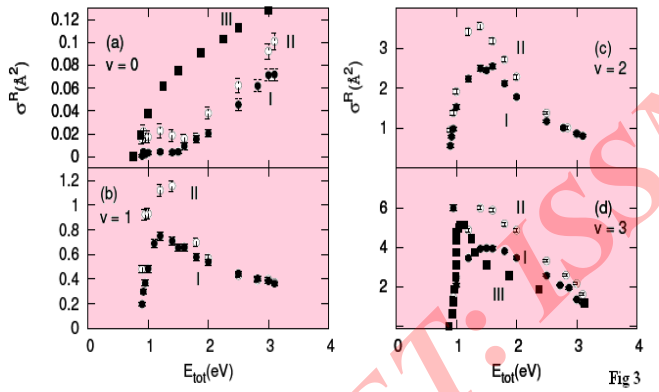

Fig 3

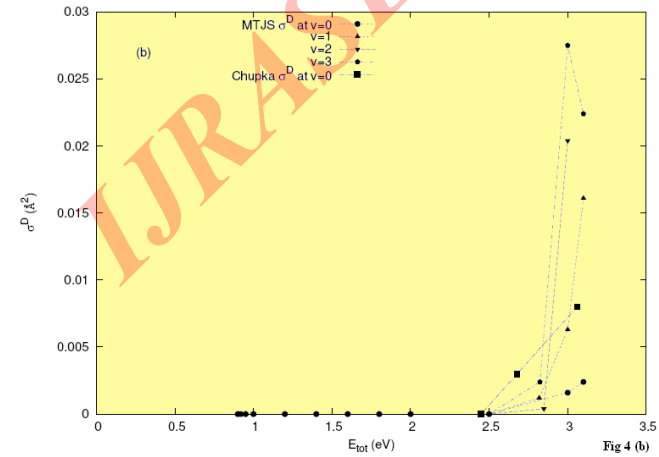

Fig 4 (b)

B. Figure Captions

Figure 1 (a). The first derivatives of diatomic potentials of AEA and JS for H_2^+ (v = 1-3, *j* =1) against interatomic distance r_{AB}.

Figure 1 (b): The 2nd derivatives of diatomic potentials of AEA and JS for H_2^+ (*v* = 1-3, *j* =1) against interatomic distance r_{AB}.

Figure 1 (c): The first derivatives of diatomic potentials of AEA and JS for HeH^+ (*v* = 1-3, *j* =1) against interatomic distance r_{AB}.

Figure 1 (d): The 2nd derivatives of diatomic potentials of AEA and JS for HeH^+ (*v* = 1-3, *j* =1) against interatomic distance r_{AB}.

Figure 2: σ^R (in Å^2) for HeH_2^+ (*v* = 0-3, *j* =1) plotted against E_{tot} (in eV) for different *v* states

Figure 3 The excitation functions (in Å^2) as functions of E_{tot} (eV) for reaction (1) with (a) H_2^+ (*v* = 0, *j* =1), (b) H_2^+ (*v* = 1, *j* =1), (c) H_2^+ (*v* = 2, *j* =1), (d) H_2^+ (*v* = 3, *j* =1). Theoretical results: ●, present; ○, MTJS. Experimental: ■, CRB [4-6].

Figure 4 The excitation functions (in Å^2) as functions of E_{tot} (eV) for reaction (2) with H_2^+ (*v* = 0 - 3, *j* =1) for (a) AEA PES and (b) MTJS PES. Theoretical results: ●, present; ○, MTJS. Experimental: ■, CRB [4-6].

ν	Chupka et al[1]	PFI-PESICO[2]	MTJS[3]	Present[4]
0	0.13	0.16	0.10	0.07
1	0.30	0.25	0.44	0.36
2	0.60	0.36	0.86	0.81
3	1.30	0.39	1.60	1.18

Table 1. σ^R at E_{tot} = 3.1 eV for various ν values

ν	Chupka et al[1]	PFI-PESICO[2]	MTJS[3]	Present[4]
0	0.16	-	-	-
1	0.60	-	1.16	0.75
2	3.60	-	3.50	2.54
3	5.30	-	5.98	3.95

Table 2. Peak value of σ^R for various ν values

[1] Reference [4-5]; σ^R at E_{tot} = 3.1 eV

[1] Reference [19]; σ^R at E_{tot} = 3.1 eV

[1] These values as calculated here are slightly different from those of References [22, 24]

[1] After AEA [25, 27]

III. RESULTS AND DISCUSSIONS

T Asymptotic behaviour of the potential derivatives

Figure 1(a) shows the first derivatives of diatomic potentials of JS and AEA for H_2^+ plotted against interatomic distances r_{AB}, while Figure 1(c) shows them for HeH^+. As expected, in both H_2^+ and HeH^+ cases the maxima occur at different r_{AB} and have different values, the AEA (HeH^+) potential maximum being about 1.3 eV lower while that for H_2^+ being about 0.9 eV lower than the corresponding MTJS value. Both the derivatives for both H_2^+ and HeH^+ behave smoothly and the plot for HeH^+ shows a maximum at around 1.0 Å and has zero value at the crossing seam at about 0.8 Å. The latter is the equilibrium distance and is thus predicted equally by both JS and AEA potentials. Then the derivatives decay to about zero value at around 3.0 Å. The H_2^+ derivatives have zero value at the crossing seam at about 1.0 Å [Figure 1(a)], which is the equilibrium distance here and show a maximum at around 1.6 Å and then they smoothly change to zero value at around 5.0 Å. Both the derivatives behave similarly at critical points and so the diatomic potentials are equally good representations at these points. However, they have slightly different analytical properties as shown above, at intermediate points and these can only affect the Hamilton's solutions. This affects the trajectory classification so much so that the values of cross sections, as we shall see below for reactions (1) and (2), are obtained sometimes on either side of the experimental plot.

Figure 1(b) shows the smooth variation of 2nd derivatives of diatomic potentials of JS and AEA for H_2^+. Here a minimum occurs at about 1.2 Å which is about 2.7 eV lower for MTJS surface. While Figure 1(c) shows that for HeH^+ at about.2.3 Å and MTJS's minimum is located 0.8 eV lower than AEA's one. The crossing seam can be seen at around 0.0 eV at about 1.0 Å. Here also the distance dependence behaviour of the two derivatives is more or less alike, but analytical properties differ as in the case of 1st derivatives. Thus the classification of trajectories and hence the excitation function is expected to be different in two cases.

Excitation functions (σ^R and σ^D)

We have investigated the reaction (1) on the surface of AEA and examined the variations of scattering cross sections (σ^R) for first four vibrational states (E_{vib} = 0.14323, 0.41835, 0.67836 and 0.92325 eV) over a wide range of E_{trans} such that

$$0.9 \leq E_{tot} \leq 3.1 \text{ eV} \qquad (3)$$

as shown in Figure 2 where we have also given selective Chupka's values of σ^R for v=0 and v=3. The equality or inequality restriction (3) arises from the covered energy range of 3.15 eV in generating the fit V^0_6, to the *ab initio* points [27].

Basic feature of the excitation function σ^R namely: (i) The vibrational enhancement, (ii) The decay of σ^R with E_{tot}, (iii) The peaks of the excitation functions and (iv) the magnitudes of σ^R for different v states, all agree with experiment fairly. To compare the relative accuracy of the AEA and JS surfaces we have tried to reproduce the results of JS [22] at the same energies so as to compare the values of σ^R obtained by the two surfaces. These σ^R values are plotted in Figures from 3(a) to 3(d) for v=0 to v=3 respectively. The two surfaces are not of equal accuracy when compared to experiment. Sometimes one is more accurate than the other in a different vibrational state.

The surface of AEA was used also to study reaction (2). We examined the variations of scattering cross sections (σ^D) for the four vibrational states as noted above, over the same range of E_{tot} as shown in Figure 4(a) and have tried to reproduce the results of KS [24] at the same energies so as to compare the values of σ^D obtained by the two surfaces. The result obtained from MTJS surface is shown in Figure 4(b). They are also given in Table 1 for a detailed comparison.

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The surface of AEA was used also to study reaction (2). We examined the variations of scattering cross sections (σ^D) for the four vibrational states as noted above, over the same range of E_{tot} as shown in Figure 3(a) and have tried to reproduce the results of KS [24] at the same energies so as to compare the values of σ^R and σ^D obtained by the two surfaces. The results obtained from MTJS surface are shown in Figure 3(b).

IV. Conclusions

Based on electronic structure of the title system, the authors have examined the analytical behaviour of its potential functions and first and second derivatives of PE of MTJS and AEA for the diatomics H_2^+ (v, j =1) and HeH^+. It has been observed that the diatomic potential energy obtained by the three methods match exactly. But their derivatives have somewhat different analytical properties as discussed above. Thus despite all the progress that has been made, the need for a re-parameterization of the potential polynomials is still there.

MTJS, sixth order polynomial PES of AEA and the QCT method were used to study reactions (1) and (2) in terms of cross sections σ^R and σ^D. The results are generally in fair agreement with experiment.

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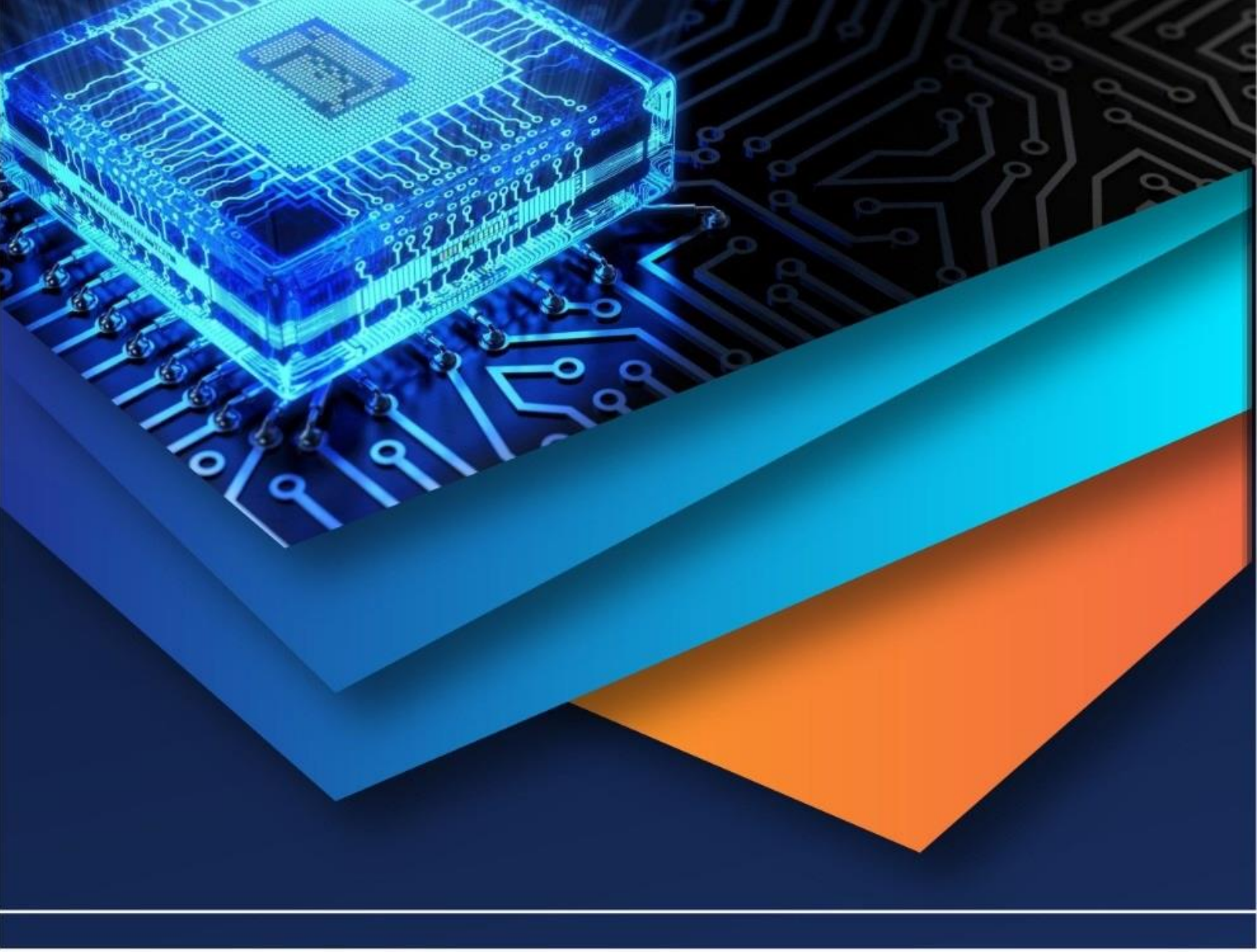

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