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Reexamination of the Origin of the Pseudo Jahn-Teller Puckering Instability in Silicene[†]

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Silicene, the graphene-like crystal formed by Si hexagonal lattice, presents a periodic buckled structure whose origin is due to the Pseudo Jahn-Teller instability on each of its planar six membered rings. This has been attributed to the coupling of the planar D_{6h} ground state with the first B_{2g} excited state through a b_{2g} vibrational mode. Here we show, by explicitly calculating the vibronic coupling constants through a complete PJT effect study, that the vibronic coupling of the ground state with only one excited state to explain the planar instability is inconsistent with the linear multilevel PJT effect theory. Furthermore, we show that in order to have consistency, the PJT model should include the next excited state, which is symmetry compatible coupled to the puckering mode. This is done by the analysis, based on DFT and TDDFT calculations, of the vibronic instability of the ground state of hexasilabenzene, the basic silicon hydrogenated hexagonal ring unit defining silicene.

Silicene, the graphene-like 2D crystal formed by Si hexagonal lattice, has attracted great theoretical interest and recently also experimentally. This has been motivated by its physical and chemical predicted properties, which are very similar to graphene and for its greater potentiality, compared to graphene, to be integrated into the silicon based electronic industry. Its synthesis has been made possible through epitaxial deposition mainly on silver substrates,^{1–5} as well as on zirconium diboride⁶ and Ir⁷ surfaces. The 2D characteristic of graphene brought an apparent paradox, since it had been proved by Peierls and Landau^{8–11} and later by Mermin and Wagner^{12,13} that due to thermodynamics instability, 2D crystals could not exist at non-zero temperature. This puzzle was solved noticing that although strictly flat 2D crystals cannot

exist, 2D structures can be stabilize through a small surface distortion in 3D, forming a corrugated 2D crystal.^{14–17}

Theoretical studies by first principle local density functional methods on the properties of free-standing silicene, carried out even before graphene was synthesized, predicted a buckled structure as opposed to the planar hexagonal aromatic structure for graphite, with a semi-metal band structure.¹⁸ More recent Density Functional Theory (DFT) calculations have confirmed the buckled structure of silicene and predicted an electron behaviour as massless Dirac Fermions and the semi-metal or zero-gap semiconductor characteristic, similar to graphene.^{19–23} Although free-standing silicene has not yet been synthesized, it has been theoretically predicted that the 2D structure is stabilized, as graphene, by an out of plane small distortion. However, the origin of the distortion in silicene is different to graphene, which presents a disordered ripple structure. From theoretical calculations, it has been widely recognized that silicene presents a periodic buckled structure whose origin resides on each of the six membered ring, simulated by hexasilabenzene. Hexasilabenzene, being the silicon analog of benzene, despite the great effort for many years trying to be synthesized (see for example^{24–26} and references therein), its study has been up to now, only theoretically.^{18,27–32} Its deformation arises from an instability of the planar hexasilabenzene structure with D_{6h} symmetry to a puckered D_{3d} structure due to the pseudo Jahn-Teller (PJT) effect, whose analysis presented so far in the literature, is based on the energy stability conditions of the puckered structured. The PJT instability has been attributed to the coupling of the planar D_{6h} ground state with just one excited state through a b_{2g} vibrational mode, arguing that the coupling to other excited states can be neglected due to their larger energy gap.^{19–22,33} However, it has been shown that the only possible instability of a non degenerate ground state arises from a PJT vibronic coupling between that particular state and one or several excited states, where the instability condition is given by the interplay of the energy gap, the vibronic coupling constant and the primary force constant of the ground state; and the relative size of the energy gaps is not an a priori argument to discard the possible couplings.^{34,35}

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[†] Electronic Supplementary Information (ESI) available: [Table S1 Standard errors for the fitting coefficients of the 4th order polynomial regression applied to the ground and excited states APES]. See DOI: 10.1039/b000000x/

In this work we present a complete PJT effect study based on DFT and TDDFT calculations, as implemented in ADF program,^{36–38} of the ground and excited states responsible for the buckled structure in silicene. This is done by analysing the puckering instability of the ground state of hexasilabenzene, the basic silicon hexagonal ring unit defining silicene. We demonstrate that the usually assumed vibronic coupling of the ground state with only one excited state to explain the planar instability of hexasilabenzene is inconsistent with the linear multilevel PJT effect theory.^{34,35} Furthermore, we show that in order to have consistency, it is necessary that the coupling should be through at least with two excited states. The analysis based on the the smallest hexagonal ring is justified from results on DFT calculations, which show that clusters gain stability on puckering when the number of rings increase from Si₆H₆ to Si₇₀H₂₂ and that the puckering distortion of hexasilabenzene is preserved in silicene sheets.³⁹

Table 1 Electronic and structural properties for the D_{6h} hexasilabenzene for different methods.^a

Functional/basis	ΔE_{HL}	d_{Si-Si}	d_{Si-H}	ω
B3LYP/TZP	3.30	2.212	1.476	-144.4i
B3LYP/TZ2P	3.31	2.208	1.475	-131.1i
B3LYP/QZ4P	3.28	2.2096	1.476	-116.6i
B1PW91/TZP	3.61	2.198	1.478	-115.1i
B1PW91/TZ2P	3.63	2.194	1.476	-97.1i
B1PW91/QZ4P	3.58	2.202	1.478	-90.1i
B3LYP*/TZP	3.0	2.212	1.479	-147.9i
B3LYP*/TZ2P	3.1	2.209	1.477	-134.8i
B3LYP*/QZ4P	3.0	2.210	1.479	-119.3i
TPSSH/TZP	2.92	2.212	1.478	-134.9i
TPSSH/TZ2P	2.94	2.208	1.477	-121.8i
TPSSH/QZ4P	2.90	2.207	1.477	-110.5i

^aHOMO-LUMO energy gap ΔE_{HL} (eV), distance Si-Si (d_{Si-Si}) and distance Si-H (d_{Si-H}) in Å, and lowest frequency ω (cm^{-1}).

In Table 1, we compare the electronic and structural properties for hexasilabenzene for 12 different functional/basis combinations. We show the results from the structure optimization calculations of the HOMO-LUMO energy gap, distance between adjacent silicon atoms d_{Si-Si} , Si-H bond lengths d_{Si-H} , and lowest frequency. The analysis is made for the hybrids GGA (B3LYP, B1PW91, B3LYP*) and hybrid meta-GGA (TPSSH) functionals in the ZORA approach with TZP, TZ2P, and QZ4P basis sets. All the calculated bond lengths d_{Si-Si} , are in the range between 2.194 and 2.212 Å, whereas the Si-H distances are between 1.475 and 1.479 Å. For the first nine methods, the HOMO-LUMO (HL) gaps are in the range between 3.0 and 3.63 eV; whereas for TPSSH HL the gaps are 2.92 eV in average. At first sight, the large HL-gaps for the D_{6h} Si₆H₆ cluster would imply molecular stability; however,

this structure has one imaginary frequency for every method, implying therefore a lack of an APES (Adiabatic Potential Energy Surface) minimum and subject to instability due to vibronic coupling. The total electronic wave function corresponds to a non-degenerate closed shell A_{1g} state, hence the hexagonal structure is not subject to a Jahn-Teller distortion. As it has been shown, the only cause of instability of non-degenerate high-symmetry configurations of molecular systems is due to the Pseudo-Jahn-Teller vibronic coupling.³⁴ For hexasilabenzene, with symmetry D_{6h}, the instability of its non-degenerate ground state can be explained as the result of a strong coupling between the ground state and one or a few excited states, which could be degenerate or quasi-degenerate with possible interaction among them under nuclear displacements.

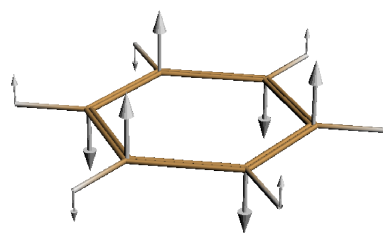


Fig. 1 Schematic diagram of the displacements of the D_{6h} b_{2g} puckering mode leading to the D_{3d} symmetric structure of Si₆H₆.

The non-degenerate b_{2g} puckering vibrational mode, which mediates the symmetry reduction D_{6h} to D_{3d} is shown in Fig 1. Here we show how this mode corresponds to the movement of the contiguous silicon atoms in opposite normal directions to the hexagonal plane, whereas the hydrogen atoms move in opposite sense. It is worth mentioning that this puckering mode coincides with the corresponding imaginary mode for hexasilabenzene. According to the theorems of Group Theory on direct product representations, the representation of the vibrational mode that mediates the coupling $\bar{\Gamma}$, must be included in the direct product of the irreducible representations (irreps) between the ground Γ , and excited state Γ' , therefore the coupling of the ground state has to be with the non-degenerate excited states with symmetry B_{2g}.

From Table 1 we notice that the calculated bond-length and HL-gap using different basis sets show similar results for the TZ2P basis than for the more expensive QZ4P, and also that the results using the B3LYP functional are between those corresponding to B1PW91 and B3LYP*. Therefore, we consider appropriate to base our analysis on the use of the B3LYP/TZ2P and TPSSH/TZ2P methods for the TDDFT calculations for the ground and excited states. We calculate the first seventy excited states for singlet to singlet transitions and the first two excited states that satisfy the condition of coupling with the ground state through a b_{2g} mode are the 12th

and 30th, for both methods, which are predominantly from the HOMO (E_{1g}) to the LUMO+2 (E_{2g}) and from the HOMO-1 (A_{2u}) to the LUMO+3 (B_{1u}), with weights 0.9933 and 0.9884 for TPSSH and 0.9965 and 0.9955 for B3LYP.

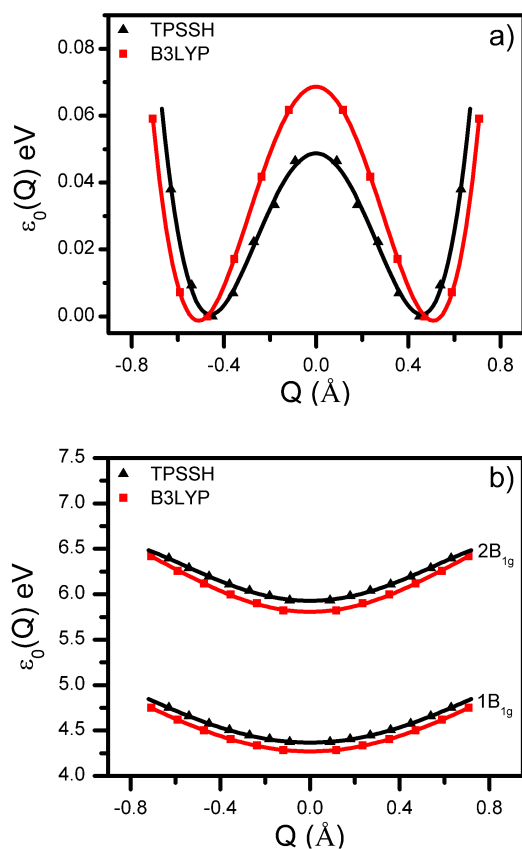


Fig. 2 APES vs puckering direction coordinate Q for both methods TPSSH and B3LYP for (a) ground state, (b) excited states.

In Fig. 2(a), (b) we show the APES profiles in eV along the Q puckering direction for ground and the first two excited states satisfying the PJT coupling condition respectively for the two methods. Table 2 presents the fitting coefficients, corresponding to a 4th-order polynomial regression applied to the ground and the two considered excited states shown in Fig. 2, including the r -square parameter (see standard errors in Table S1). As will be shown later, a general property within a PJT linear coupling model is that the quartic coefficient of the ground state should be equal to the negative of the quartic coefficient corresponding to the coupled excited states. From Table 2 we can see that a single excited state is not enough to model the ground state instability because the above mentioned property is not fulfilled, whereas if a superposition of the first two excited states is considered, the condition is ful-

Table 2 Fitting coefficients of the 4th order polynomial regression applied to the ground and excited states APES

Method	State	a_0	a_2	a_4	r
TPSSH	Ground	0.0487	-0.4595	1.0956	0.992
	1 B_{2g}	4.3667	1.0945	-0.3226	0.999
	2 B_{2g}	5.9282	1.4898	-0.7979	0.998
B3LYP	Ground	0.0687	-0.5394	1.0396	0.999
	1 B_{2g}	4.2706	1.1052	-0.3012	0.999
	2 B_{2g}	5.8075	1.5435	-0.6562	0.998

filled within a difference of 0.02 and 0.08 eV/Å⁴ for TPSSH and for B3LYP respectively. Hence, the usually assumed origin of the PJT effect in silicene reported in the literature as the coupling of the ground state with just one B_{2g} excited state, is not consistent with the PJT linear coupling model; and the D_{6h} ground state instability and the puckering mode arises as a result of the coupling with at least two B_{2g} excited states. This is a problem that pertains to the linear multilevel PJT effect,^{34,35} where at least two excited states contribute to the ground state instability. Within the linear coupling model, the APES for three states, which are the solutions of the vibronic equations, are given by the secular equation

$$\begin{vmatrix} \frac{1}{2}K_0Q^2 - E & f_1Q & f_2Q \\ f_1Q & \frac{1}{2}K_1Q^2 + 2\Delta_1 - E & 0 \\ f_2Q & 0 & \frac{1}{2}K_2Q^2 + 2\Delta_2 - E \end{vmatrix} = 0 \quad (1)$$

where $2\Delta_i$ ($i = 1, 2$) are the energy gaps between the ground state and the i th excited state at $Q = 0$, K_i are the primary force constants, and f_i are the linear coupling constants:

$$f_i = \langle 0 | \frac{\partial V(Q)}{\partial Q} | i \rangle \quad (2)$$

being V the electron-nucleon interaction operator. Making a series expansion of the solution of the Eq. (1) around $Q = 0$ up to quartic terms in Q , the APES for the excited states around the high-symmetry configuration are

$$E_1 = 2\Delta_1 + \frac{1}{2}(K_1 + \Gamma_1)Q^2 - \frac{1}{8\Delta_1}[\Gamma_1^2 + \Gamma_1(K_1 - K_0) + \Gamma_1\Gamma_2\frac{\Delta_2}{\Delta_2 - \Delta_1}]Q^4 + \dots \quad (3)$$

and

$$E_2 = 2\Delta_2 + \frac{1}{2}(K_2 + \Gamma_2)Q^2 - \frac{1}{8\Delta_2}[\Gamma_2^2 + \Gamma_2(K_2 - K_0) + \Gamma_1\Gamma_2\frac{\Delta_1}{\Delta_2 - \Delta_1}]Q^4 + \dots \quad (4)$$

where

$$\Gamma_i = |f_i|^2/\Delta_i \quad (5)$$

The coupled ground state curvature K and quartic term coefficient β_0 are then expressed as a superposition of the contributions of the two excited states and are given by

$$K = K_0 - \sum_i \Gamma_i \quad (6)$$

$$\beta_0 = - \sum_i \beta_i \quad (7)$$

where β_i are the quartic terms in Eqs. (3), (4)); and the ground state APES can be written as

$$E_0 = \frac{K}{2} Q^2 + \beta_0 Q^4 \quad (8)$$

As can be seen from Eqs. (3) and (4), the quartic term β_i is composed of three terms. The first one determines the influence of the corresponding excited state over the ground state due to the PJT vibronic coupling. The second term is also present when the coupling is through only one state and it is zero only when the primary force constants K_0 and K_1 are equal. The third term corresponds to the case when the two excited states are coupled to the ground state by the same normal mode and therefore coupled to each other and may become very important when the excited states are quasidegenerate. The first and third terms are always negative, favouring therefore the ground state instability; whereas the second term can be positive or even negative, depending on the relative values of $K_{1,2}$ and K_0 .

From Eq. (7) we can see that when $i = 1$, i.e., when we have just the coupling of the ground state with one excited state, the ground state quartic coefficient should be the negative of the excited state quartic coefficient. As it was mentioned before, this condition is not satisfied by the quartic coefficients of Table 2 when a single excited state is considered. The APES defined by Eqs. (3), (4) and (8) can be simultaneously satisfied by equating their quadratic and quartic terms with the respective coefficients of the polynomial regression (Table 2). The five unknown parameters: K_0, K_1, K_2, Γ_1 , and Γ_2 were calculated solving the resulting non-linear equation system through an iterative method. In Table 3 are presented the JT gain, APES minimum position, the semi-gaps, and the numerically averaged curvatures and vibronic coupling constants.

As can be seen from the results of Table 3, the instability conditions

$$\sum_i \Gamma_i = \sum_i |f_i|^2 / \Delta_i > K_0 \quad (9)$$

are satisfied for both methods.

Conclusions

In conclusion, we have presented a complete PJT effect study, based on DFT and TDDFT calculations, of the ground and excited states responsible for the buckled structure in silicene.

Table 3 Calculated vibronic coupling parameters

Parameter	TPSSH	B3LYP
JT gain (meV)	48.75	68.29
Ground State APES minimum $Q_0(\text{\AA})$	0.46	0.51
Semi-gap Δ_1 (eV)	2.18	2.14
Semi-gap Δ_2 (eV)	2.96	2.90
Ground state primary K_0 (eV/ \AA^2)	6.57	5.81
1st excited state primary K_1 (eV/ \AA^2)	-3.91	-3.47
2nd excited state primary K_2 (eV/ \AA^2)	1.59	1.87
Off-diagonal linear vibronic constant F_1	3.65	3.50
Off-diagonal linear vibronic constant F_2	2.03	2.21
Γ_1 (eV/ \AA^2)	6.10	5.68
Γ_2 (eV/ \AA^2)	1.39	1.22

This was done by analysing the puckering instability of the ground state of hexasilabenzene, the basic silicon hexagonal ring unit defining silicene. We demonstrated that the usually assumed vibronic coupling of the ground state with only one excited state to explain the planar instability of hexasilabenzene is inconsistent with the linear multilevel PJT effect theory, and that in order to have consistency, it is necessary that the coupling should be through at least with two excited states. This coupling might have implications on the optical and functionalization properties of silicene.

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