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Modulation of Nearly Free Electron States in Hydroxyl-Functionalized MXenes: A First-Principles Study

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I. THE SOLUTIONS OF IMAGE-POTENTIAL WELL

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z)+V(z)\psi(z)=E\psi(z) \tag{1}$$

where

$$V(z)=\begin{cases}-V_0 & |z|\le a \quad (2)\\ -\dfrac{e^2}{4(|z|-a+\Delta)} & |z|>a \quad (3)\end{cases}$$

and $\Delta=\frac{e^2}{4V_0}$. The eigenstates of the Schrödinger equation are solved in different regions, respectively.

If $z<-a$, the above equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z)+\frac{e^2}{4(z+a-\Delta)}\psi(z)=E\psi(z) \tag{4}$$

Let $a_0=\frac{\hbar^2}{me^2}$ the Bohr's radius, $E_0=\frac{e^2}{2a_0}=13.6$ and $\frac{E}{E_0}=\zeta$. Eq. 4 is

$$\frac{d^2\phi(\eta)}{d\eta^2}-\frac{1}{2\eta}\phi(\eta)+\zeta\phi(\eta)=0, \tag{5}$$

where $\frac{z+a-\Delta}{a_0}=\eta$ and $\psi(z)=\psi(a_0\eta-a+\Delta)=\phi(\eta)$. Only bound states are considered, therefore $\zeta<0$. Substitute $\phi(\eta)=e^{\sqrt{-\zeta}\eta}\eta f(\eta)$ into Eq. 5, we get

$$2\eta\frac{d^2f(\eta)}{d\eta^2}+4(1+\eta\sqrt{-\zeta})\frac{df(\eta)}{d\eta}+(4\sqrt{-\zeta}-1)f(\eta)=0 \tag{6}$$

If we assume $\eta=-\frac{1}{2\sqrt{-\zeta}}\rho$ and $f(\eta)=f(-\frac{1}{2\sqrt{-\zeta}}\rho)=F(\rho)$, the above equation becomes

$$\rho\frac{d^2F(\rho)}{d\rho^2}+(2-\rho)\frac{dF(\rho)}{d\rho}-(1-\frac{1}{4\sqrt{-\zeta}})F(\rho)=0 \tag{7}$$

This is confluent hypergeometric equation or Kummer's equation,[1] which has two independent solutions.

$$F(\rho)=AU(1-\frac{1}{4\sqrt{-\zeta}},2,\rho)+B_1F_1(1-\frac{1}{4\sqrt{-\zeta}},2,\rho) \tag{8}$$

where A and B are constants to be determined, ${}_1F_1(1-\frac{1}{4\sqrt{-\zeta}},2,\rho)$ is the Kummer's function[1] and this solution is nonsense because $e^{\sqrt{-\zeta}\eta}\eta_1F_1(1-\frac{1}{4\sqrt{-\zeta}},2,-2\sqrt{-\zeta}\eta)$ is infinitive if $\eta\to-\infty$. Thus the only possible solution is $U(1-\frac{1}{4\sqrt{-\zeta}},2,\rho)$, which is Tricomi's function.[1] The finial solution of Eq. 4 is

$$\psi_1(z)=Ae^{\frac{\sqrt{-\zeta}(z+a-\Delta)}{a_0}}\frac{z+a-\Delta}{a_0}U\left(1-\frac{1}{4\sqrt{-\zeta}},2,\frac{-2\sqrt{-\zeta}(z+a-\Delta)}{a_0}\right). \tag{9}$$

where A is a constant to be determined.

In the middle area ($|z| \leq a$), the potential is $-V_0$ and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z) - V_0(z)\psi(z) = E\psi(z) \tag{10}$$

Using the Bohr's radius and Rydberg unit of energy in the above equation and let $\eta = \frac{z}{a_0}$, we get

$$\frac{d^2\phi(\eta)}{d\eta^2} + k^2\phi(\eta) = 0 \tag{11}$$

where $k^2 = \frac{E+V_0}{E_0}$ and the solution is

$$\psi_2(z) = B\sin(k\frac{z}{a_0}) + C\cos(k\frac{z}{a_0}) \tag{12}$$

where B and C are constants to be determined.

If $z > a$, the solving process is very similar to the previous one and the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z) - \frac{e^2}{4(z-a+\Delta)}\psi(z) = E\psi(z) \tag{13}$$

By using Bohr's radius and Rydberg unit of energy, we find

$$\frac{d^2\phi(\eta)}{d\eta^2} + \frac{1}{2\eta}\phi(\eta) + \zeta\phi(\eta) = 0 \tag{14}$$

where $\frac{z-a+\Delta}{a_0} = \eta$ and $\psi(z) = \psi(a_0\eta + a - \Delta) = \phi(\eta)$. By comparison, we find we can get Eq. 5 from Eq. 14 by the substitution $\eta \to -\eta$. Therefore, the corresponding solution is

$$\psi_3(z) = De^{\frac{-\sqrt{-\zeta}(z-a+\Delta)}{a_0}}\frac{z-a+\Delta}{a_0}U\left(1-\frac{1}{4\sqrt{-\zeta}}, 2, \frac{2\sqrt{-\zeta}(z-a+\Delta)}{a_0}\right). \tag{15}$$

where D is an undetermined constant.

Given the fact that the potential well is symmetric, the wave functions have even or odd parities, respectively. As a result, only two undetermined constants are independent. For example, if the wave function is even, $B = 0$ and $D = -A$. The constants A and C can be determined when the conditions on continuity of the wave function and its derivatives are applied, i.e.

$$\psi_1(-a) = \psi_2(-a) \tag{16}$$

$$\frac{d\psi_1(-a)}{dz} = \frac{d\psi_2(-a)}{dz} \tag{17}$$

With the differentiation equality $\frac{dU(a,b,z)}{dz} = -aU(a+1,b+1,z)$, the above equations are equivalent to the following matrix multiplication,

$$M^e \times V = \begin{pmatrix} M_{11} & -\cos(k\frac{a}{a_0}) \\ M_{21} & -\frac{k}{a_0}\sin(k\frac{a}{a_0}) \end{pmatrix} \times \begin{pmatrix} A \\ C \end{pmatrix} = 0 \tag{18}$$

where

$$M_{11} = -\frac{\Delta}{a_0} e^{-\frac{\sqrt{-\zeta}\Delta}{a_0}} U\left(1 - \frac{1}{4\sqrt{-\zeta}}, 2, \frac{2\sqrt{-\zeta}\Delta}{a_0}\right) \tag{19}$$

$$M_{21} = \frac{e^{-\frac{\Delta\sqrt{-\zeta}}{a_0}} \left(2\left(a_0 - \Delta\sqrt{-\zeta}\right) U\left(1 - \frac{1}{4\sqrt{-\zeta}}, 2, \frac{2\Delta\sqrt{-\zeta}}{a_0}\right) + \Delta\left(1 - 4\sqrt{-\zeta}\right) U\left(2 - \frac{1}{4\sqrt{-\zeta}}, 3, \frac{2\Delta\sqrt{-\zeta}}{a_0}\right)\right)}{2{a_0}^2} \tag{20}$$

The determinant of matrix M^e (namely Wronskian) is energy-dependent. The constants are nonzero if and only if the determinant of matrix M^e is zero. The corresponding energies indicate the binding energies.

If the wave function has the odd parity, $C = 0$ and $D = A$, and Eq.21 becomes

$$M^o \times V = \begin{pmatrix} M_{11} & \sin(k\frac{a}{a_0}) \\ M_{21} & -\frac{k}{a_0}\cos(k\frac{a}{a_0}) \end{pmatrix} \times \begin{pmatrix} A \\ B \end{pmatrix} = 0 \tag{21}$$

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[1] F. W. J. Olver, D. W. Lozier, R. F. Boisvert and C. W. Clark, NIST Handbook of Mathematical Functions (Cambridge University Press, New York, 2010).

Captions

: FIG. S1 The energy bands with respect to different interlayer distances were calculated by using PBEh (red), HSE06 (blue) and PBE (yellow).

: FIG. S2 The response of energy bands to the electric fields. The distance between the neighboring layers is 50 Å. When the field is about 0.08eV/Å, the exchange of NFE states happens.

: FIG. S3 The response of energy bands to the electric fields. The distance between the neighboring layers is 40 Å.

: FIG. S4 The response of energy bands to the electric fields. The distance between the neighboring layers is 30 Å.

: FIG. S5 The response of energy bands to the electric fields. The distance between the neighboring layers is 20 Å.

: FIG. S6 The response of energy bands to the electric fields. The distance between the neighboring layers is 15 Å.

: FiIG. S7 The energy band gap widths responses to the electric fields, calculated by PBEh (a), HSE06 (b) and PBE (c). The interlayer separation is 20 Å, and all results are calculated by VASP.

: FIG. S8 (a) The calculated energy gap widths responses to the electric fields by ATK, and the distance between the neighboring layers is 20 Å. The structures used in calculations with (b) and without (c) ghost atoms. The grey atoms represent the ghost atoms.

TABLE S1. The relative energies (in the unit of eV) of three stable structures (BB, AB and AA) calculated from PBEh and HSE06, respectively. BB structure is the reference structure and all energies are relative to it.

sites of OH	BB	BA	AA	TB	TA	TT
PBEh	0.000	0.422	0.883	1.564	2.081	2.818
HSE06	0.000	0.347	0.766	1.557	2.072	2.806

TABLE S2. The band gap width (in the unit of eV) evolution with respect to the vacuum size (in the unit of Å).

vacuum size(Å)	120	60	30	20	18	15
gap width(eV)	0.46	0.46	0.45	0.43	0.40	0.30

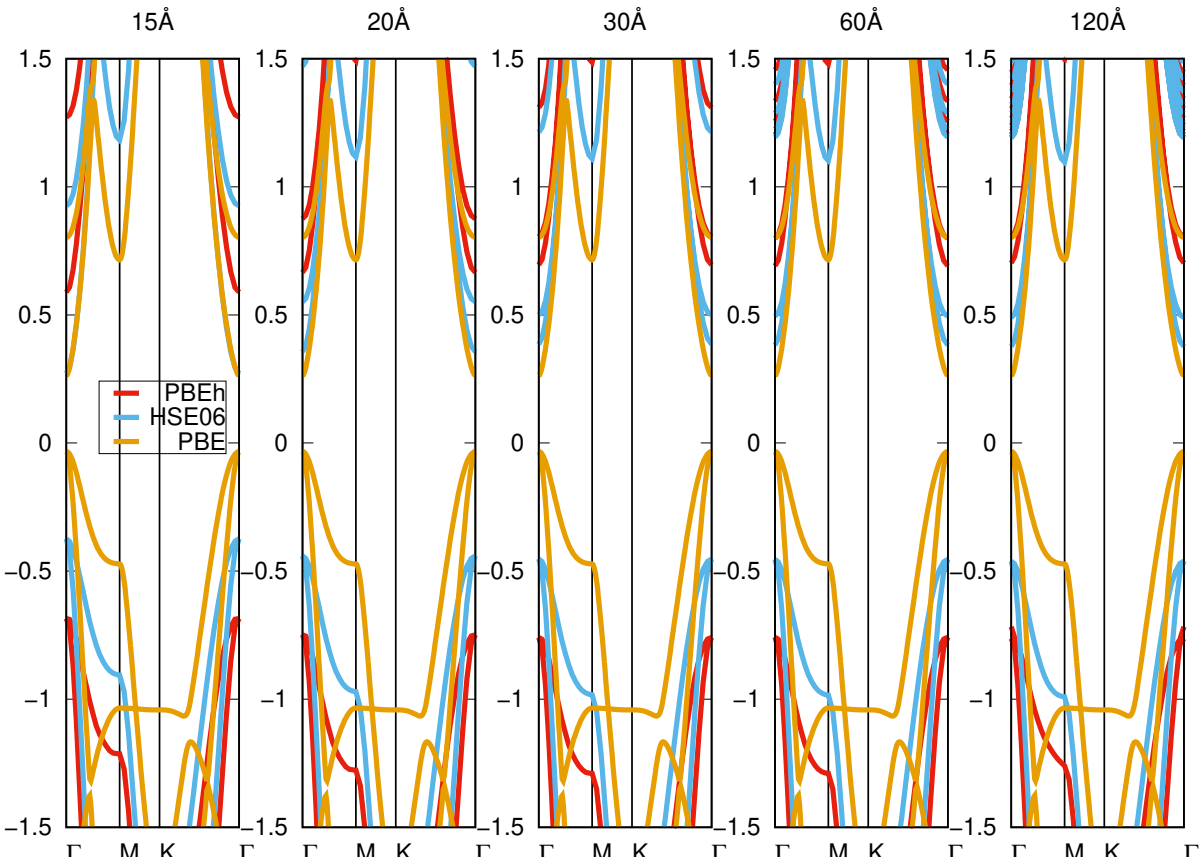

FIG. S1. J. Zhou et al.

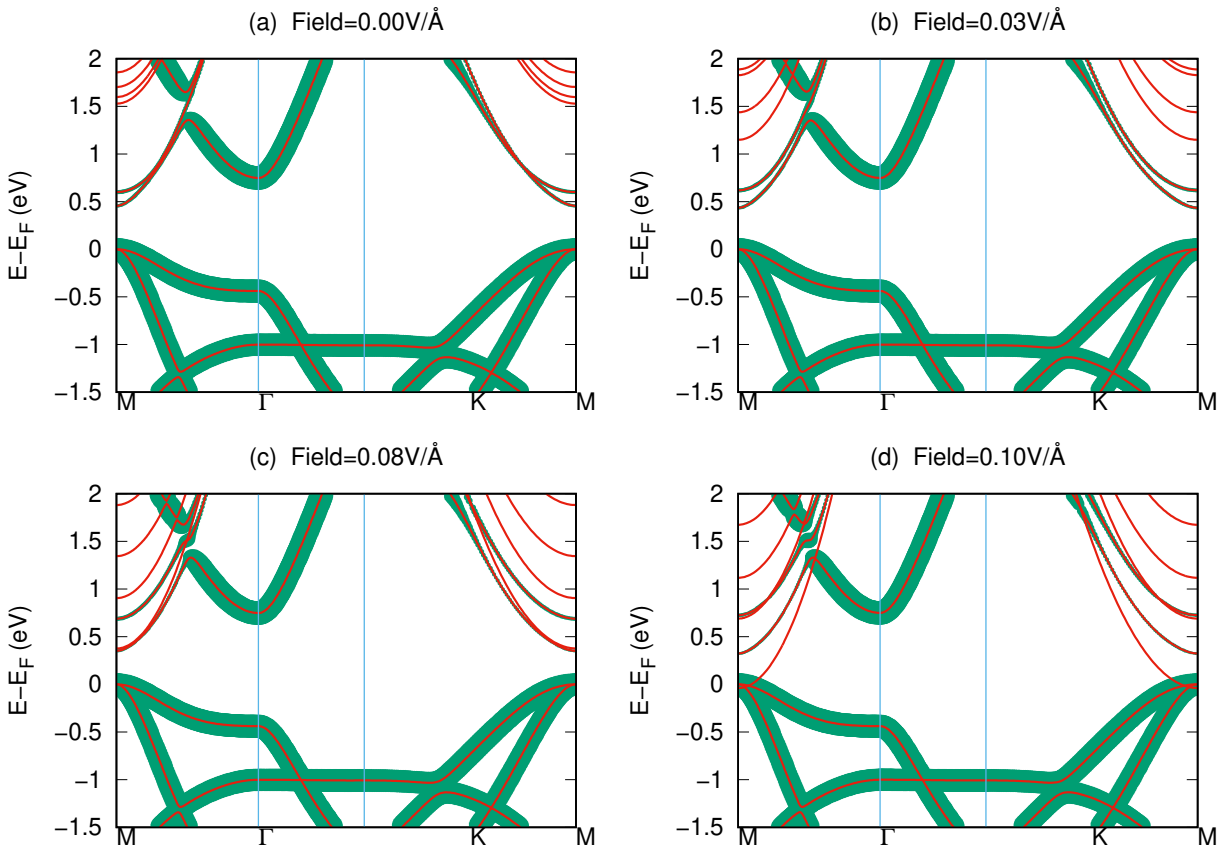

FIG. S2. J. Zhou et al.

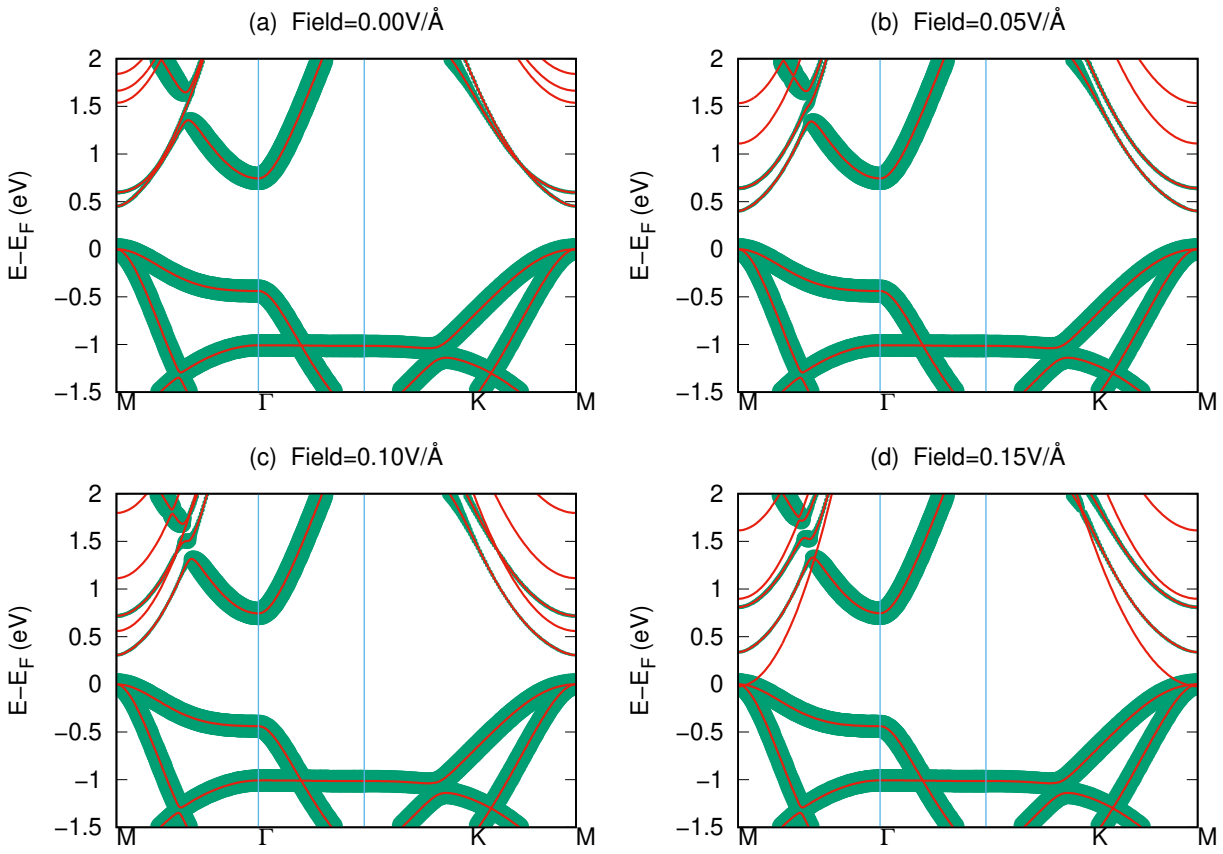

FIG. S3. J. Zhou et al.

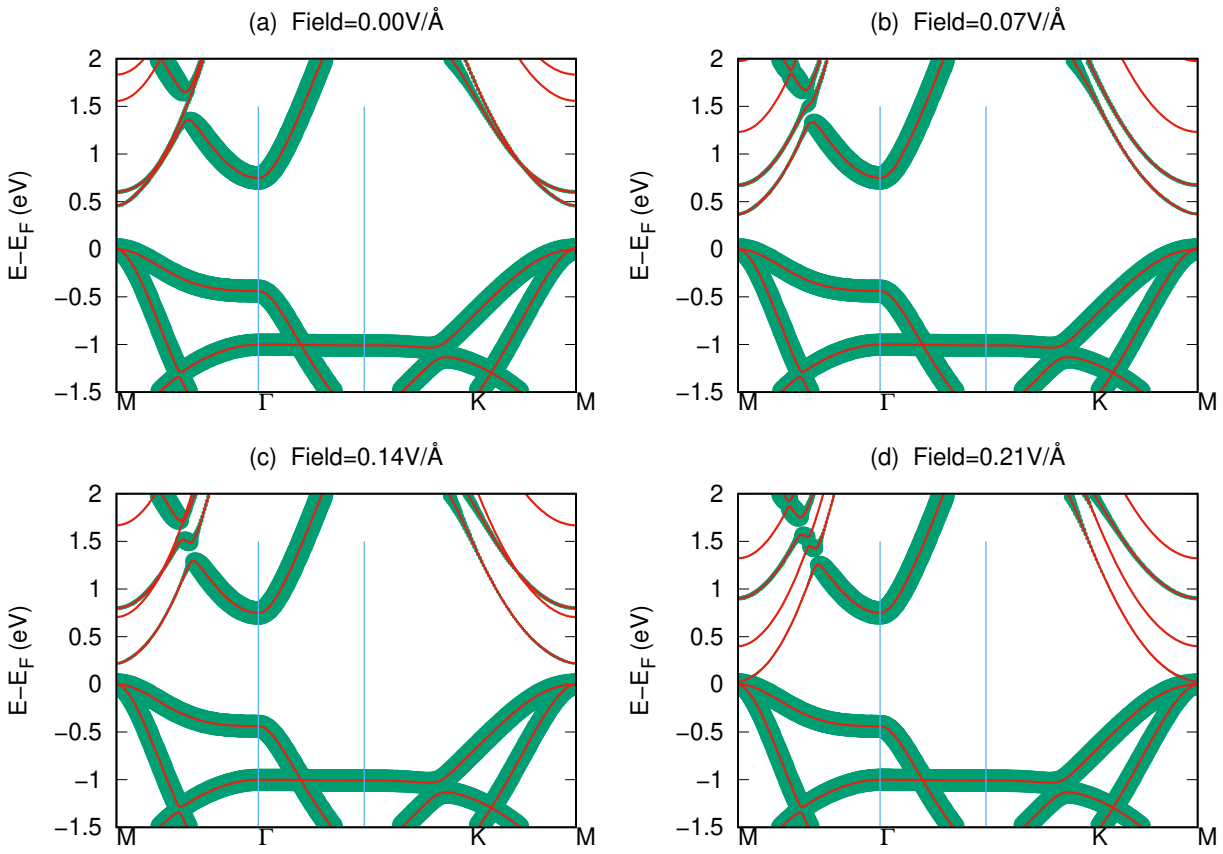

FIG. S4. J. Zhou et al.

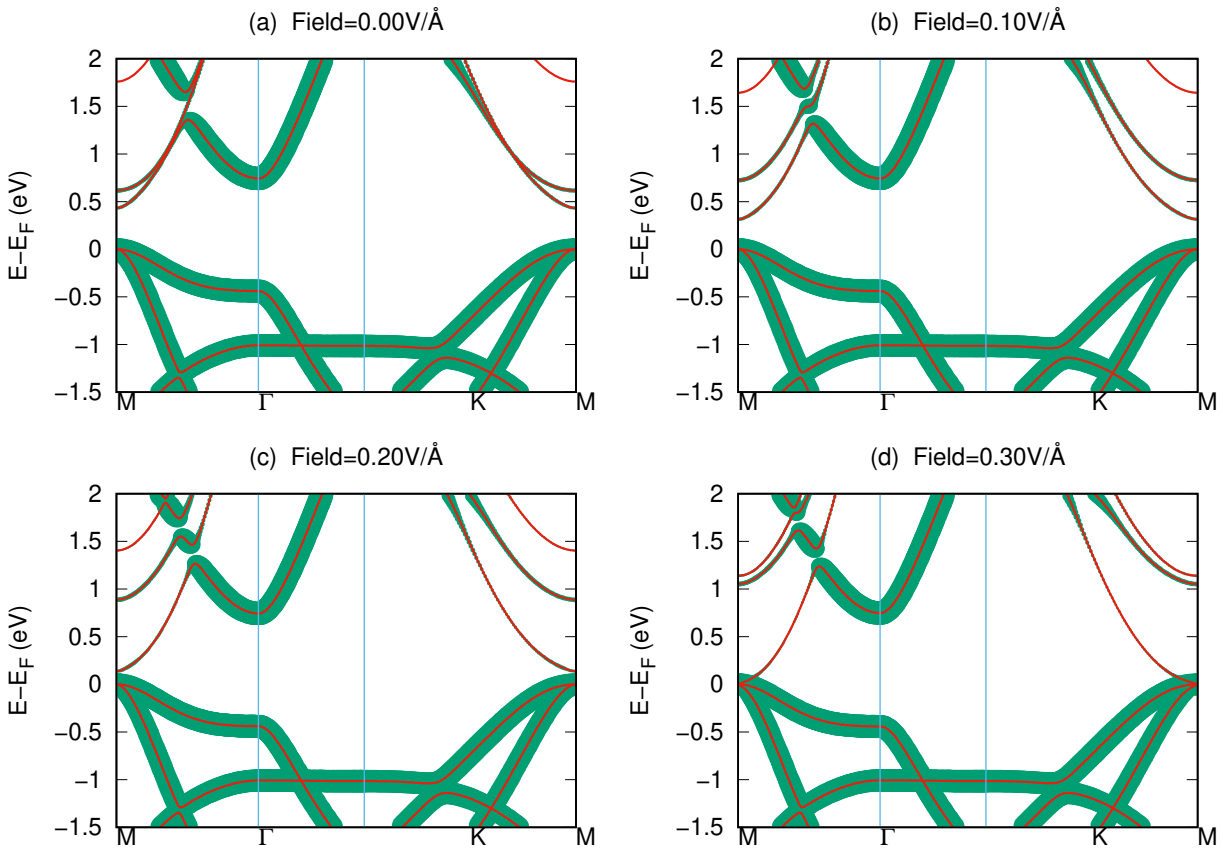

FIG. S5. J. Zhou et al.

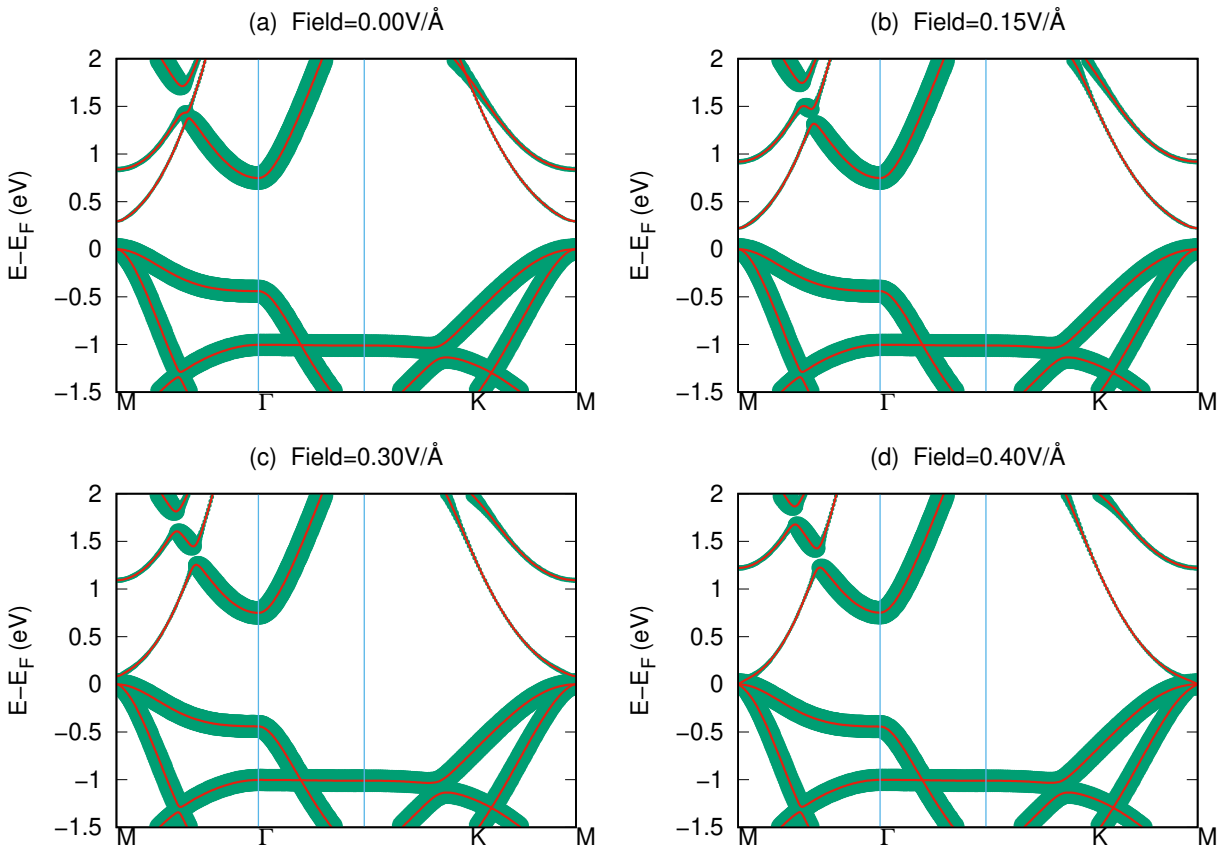

FIG. S6. J. Zhou et al.

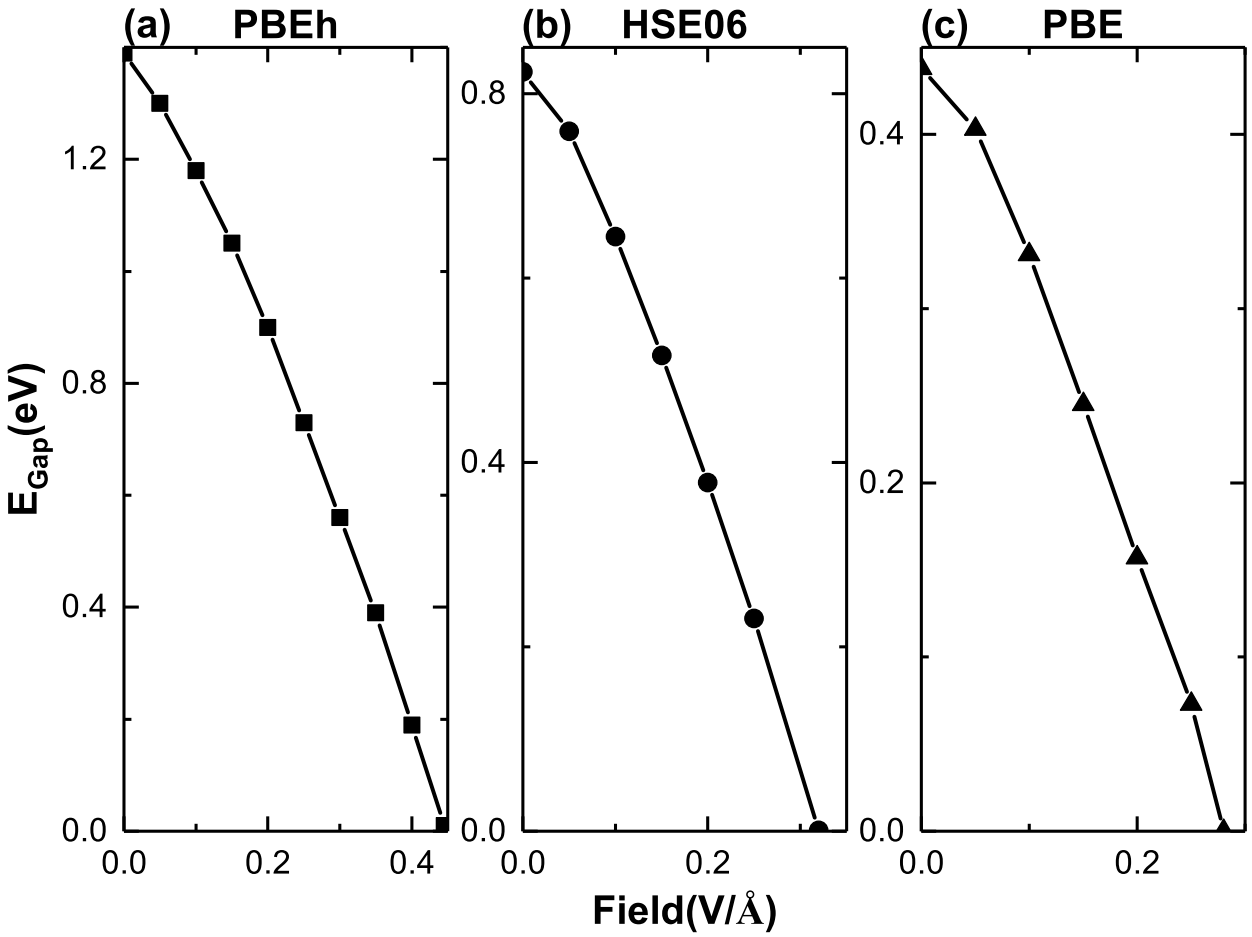

FIG. S7. J. Zhou et al.

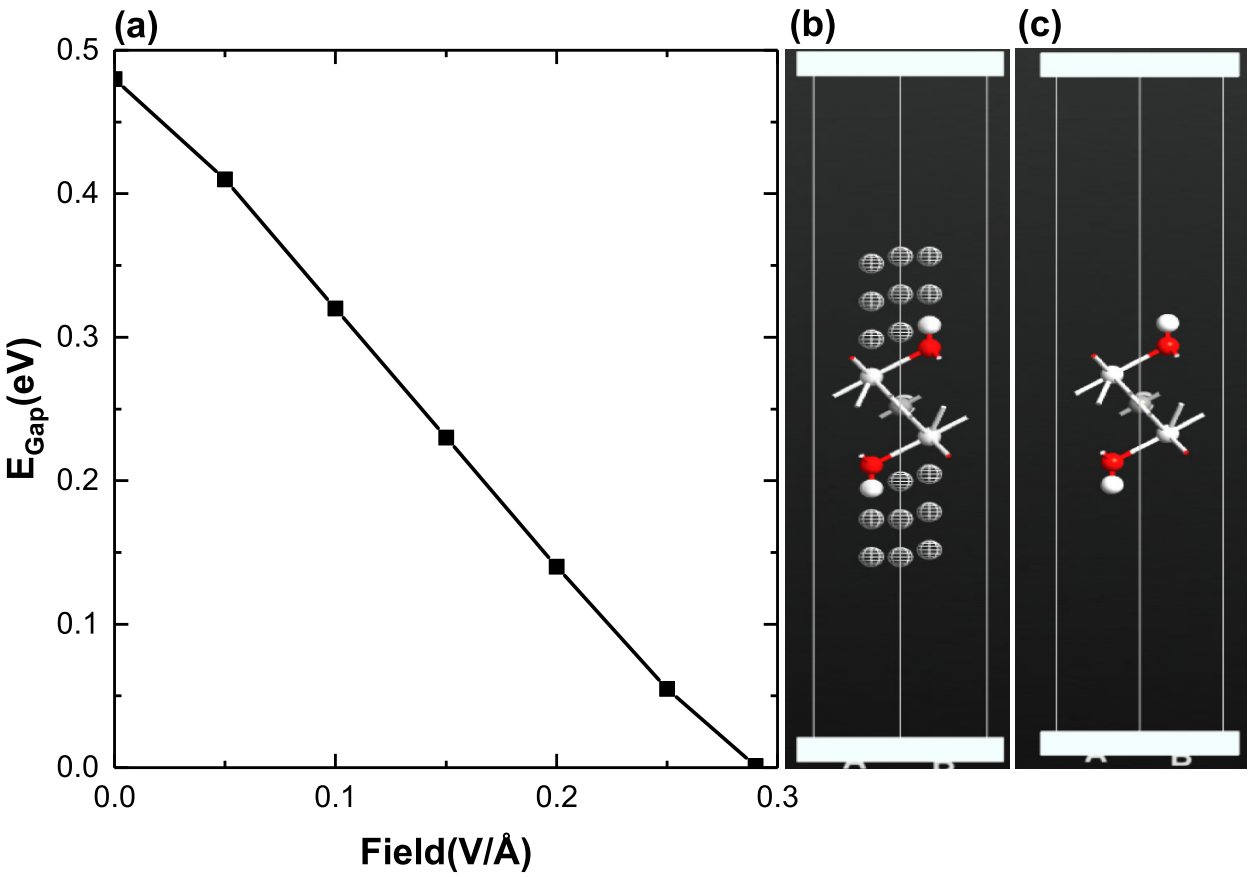

FIG. S8. J. Zhou et al.