Supporting information–Low Density of Conduction and Valence Band States Contribute to the High Open-Circuit Voltage in Perovskite Solar Cells

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Method choosing

In order to obtain relative more accurate DOS, GGA-PS functional,[1] GW method[2,3] and HSE06 functional[4,5] are carefully testified. GW method and HSE06 functional could give accurate results. But the computational time is massive comparing to normal DFT calculation. Therefore, we will use normal DFT if its result is comparable to that of GW method and HSE06 functional. Table S1 and Figure S1 show the band structure and effective masses of silicon. It is found that there is a large difference for band gaps between different methods. We also found that their band structure, especially the sharp are very similar, which indicates that the effective mass maybe similar. We confirm it with calculations. The effective masses are shown in Table S1. We found that the is very little differences between them. The error between GGA-PS functional and GW method are about 10%. Therefore, we use GGA-PS functional to perform our calculations.

The effective mass are obtain by fitting 5 points near the high-symmetry k-point with quadratic function. The reduced mass for silicon is defined as $m_r = (m_1 * m_2 * m_3 * .. * m_n)^{1/n}$. S points is where th the conduction band minimum locate. The band structure data was generated from Wannier90 program.[6,7]

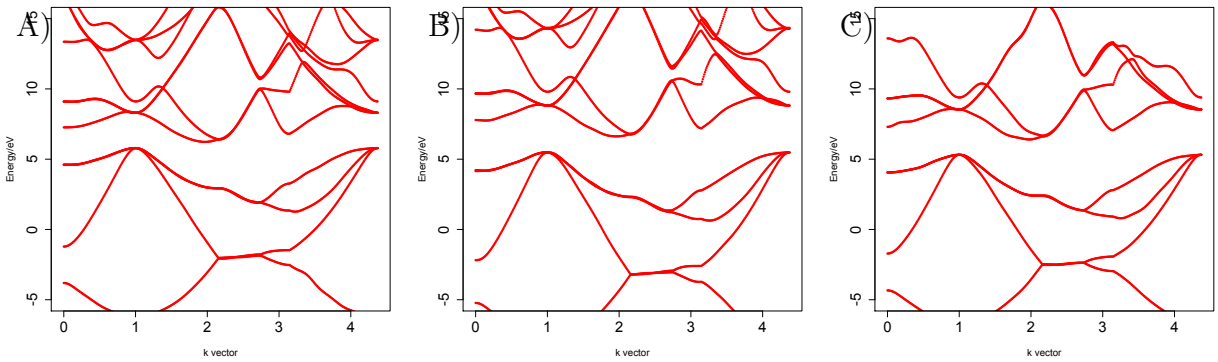

Figure S1: Band structure of silicon calculated by different methods. A) Normal DFT with PBEsol exchange function, noted as PS; B) HSE method; C) GW method. The band gaps is 0.44 eV, 1.14 eV and 1.10 eV for GGA-PS, HSE06 and GW method respectively.

Table S1: The effective masses of silicon on different directions calculated by GGA-PS, HSE06, GW methods. Unit is m_0, which is the free electron rest mass.

Method		GGA-PS	HSE06	GW
Band gap (eV)		0.44	1.14	1.10
G-S	CB	0.61	0.89	0.47
S-X	CB	0.58	1.14	0.43
Reduced mass	CB	0.59	1.01	0.45
L-Γ	VB1	-0.58	-0.42	-0.65
	VB2	-0.65	-0.68	-0.65
	VB3	-0.09	-0.12	-0.11
Γ-X	VB1	-0.45	-0.30	-0.35
	VB2	-0.27	-0.71	-0.29
	VB3	-0.14	-0.16	-0.15
K-Γ	VB1	-1.07	-0.71	-0.80
	VB2	-0.28	-0.61	-0.31
	VB3	-0.11	-0.13	-0.12
Reduced mass	VB1	0.65	0.45	0.57
	VB2	0.36	0.66	0.39
	VB3	0.12	0.14	0.12

Effective mass and DOS of Silicon

Table S2: K points and Coordinates Silicon effective masses calculation.

K points	Coordinates	K points	Coordinates
Γ	(0,0,0)	Y	(0,0.5,0)
R	(-.5,-.5,-.5)	M	(.5,0,.5)
W	(.375,.375,.75)	S	(0.417391, 0, 0.417391)
N	(.5,0,-.5)		

Table S3: Silicon effective masses and effective mass DOSs.

Bands	Γ-S	S-N	S-Y	g	M_{eff}	DOS of band	Total DOS	Product
CB	1.04	0.19	0.25	6	1.20	3.35×10^{19}	3.35×10^{19}	
	R-G	G-M	W-G					
VB1	-0.64	-0.26	-2.70	1	0.76	1.69×10^{19}		7.76×10^{38}
VB2	-0.64	-0.26	-0.25	1	0.35	5.18×10^{18}	2.32×10^{19}	
VB3	-0.10	-0.17	-0.11	1	0.12	1.10×10^{18}		

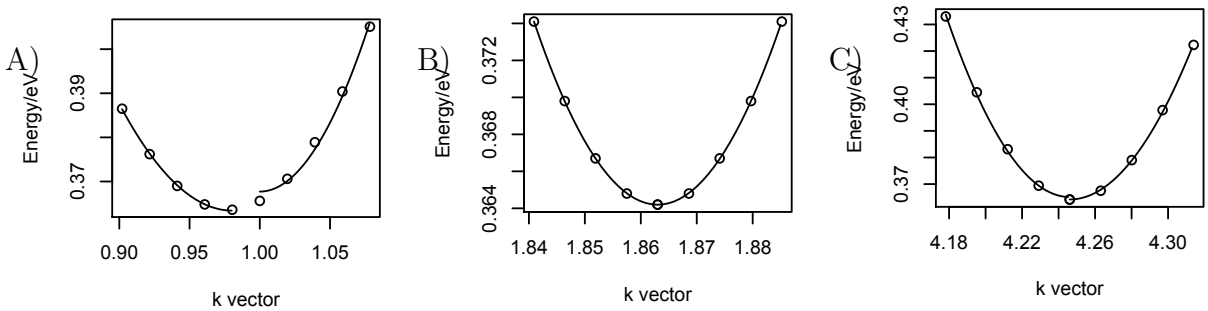

Figure S2: Silicon Conduction band near S point on the direction of A) Γ-S; B) S-N; C) S-Y and its fitting for mass evaluation. Only left half is the wanted fitting. This plot calculation is specially performed for the effective mass calculation of S point. High density points near S points are implemented. Energy levels are raised.

Effective mass of α-$FAPbI_3$

Table S4: α-$FAPbI_3$ effective masses and effective mass DOSs

Bands	M-Z	Z-Γ	Energy	g	M_{eff}	DOS of band	Total DOS	Product
CB3	0.12	0.17	0.77	2	0.21	2.51×10^{18}		
CB2	0.28	0.16	0.73	2	0.37	5.60×10^{18}	1.20×10^{19}	3.47×10^{37}
CB1	0.17	0.23	0.69	2	0.30	4.24×10^{18}		
VB	-0.14	-0.16	-0.68	2	0.24	2.90×10^{18}	2.90×10^{18}	

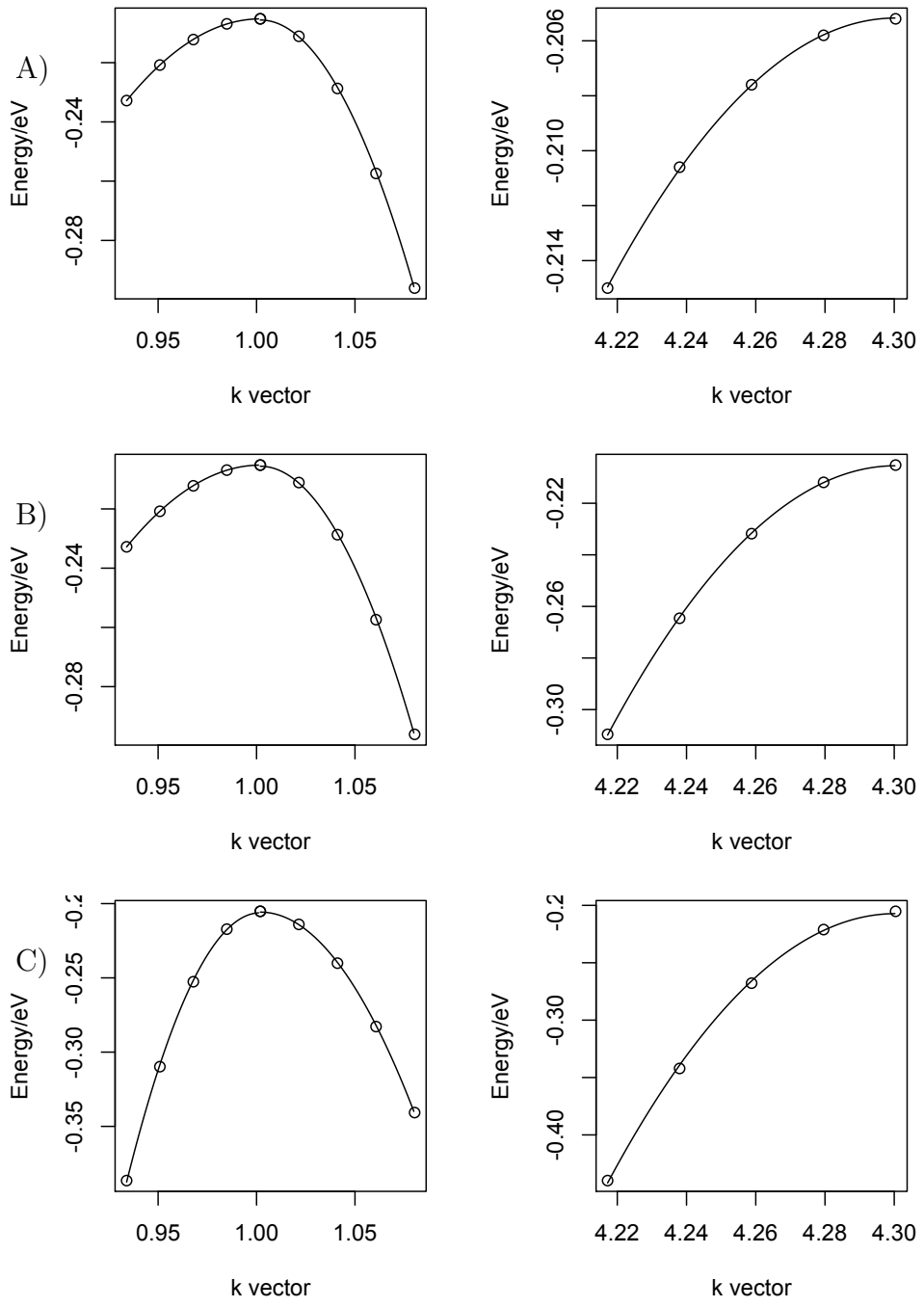

Figure S3: Silicon Valence band near Γ point on the direction of R-Γ, Γ-M, W-Γ of A) VB1; B) VB2; C) VB3 and its fitting for mass evaluation.

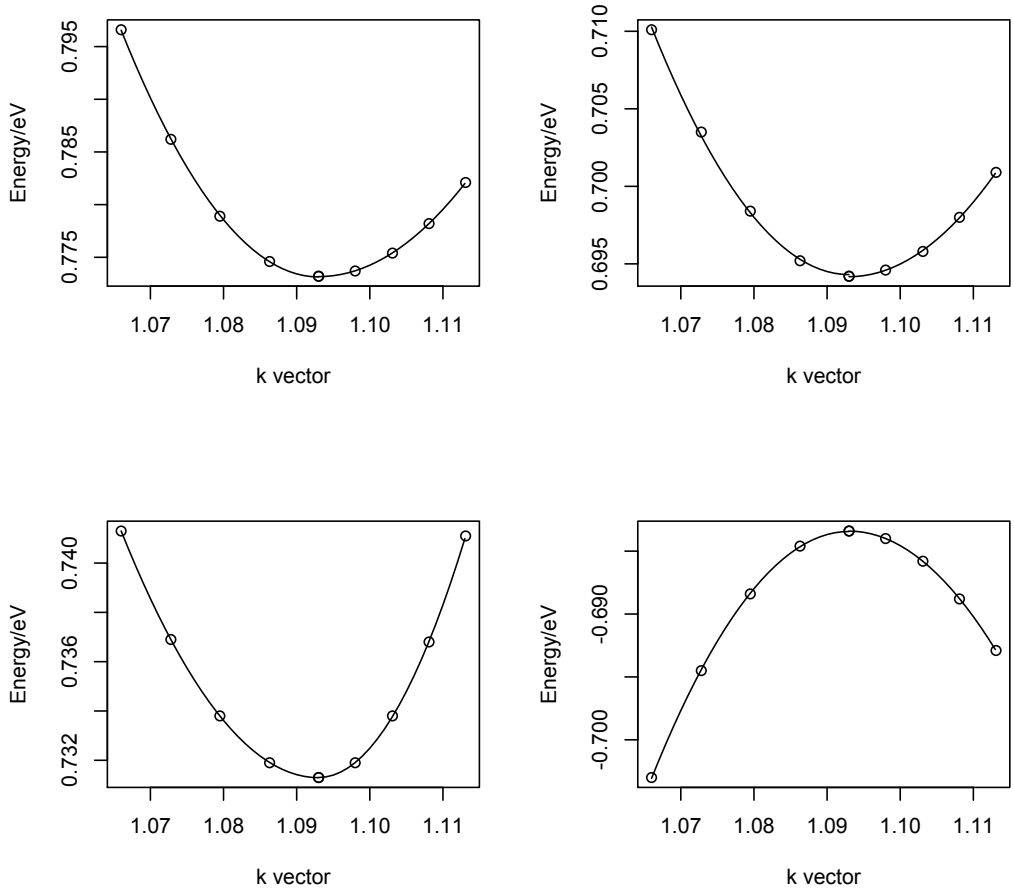

Figure S4: α-$FAPbI_3$ CB3, CB2, CB1 and valence band near Z point on the direction of M-Z (left half), Z-Γ (right half) and its fitting for mass evaluation.

Effective mass of $MAPbCl_3$

Table S5: $MAPbCl_3$ effective masses and effective mass DOSs.

Bands	Z-Γ	Γ-X	Γ-R	Energy	g	M_{eff}	DOS of band	Total DOS	Product
CB3	0.11	0.30	0.19	1.63	1	0.18	2.00×10^{18}		
CB2	1.36	0.14	0.21	1.49	1	0.34	5.08×10^{18}	1.36×10^{19}	4.94×10^{37}
CB1	0.70	0.35	0.31	1.45	1	0.42	7.00×10^{18}		
VB	-0.32	-0.24	-0.26	-0.85	1	0.27	3.64×10^{18}	3.64×10^{18}	

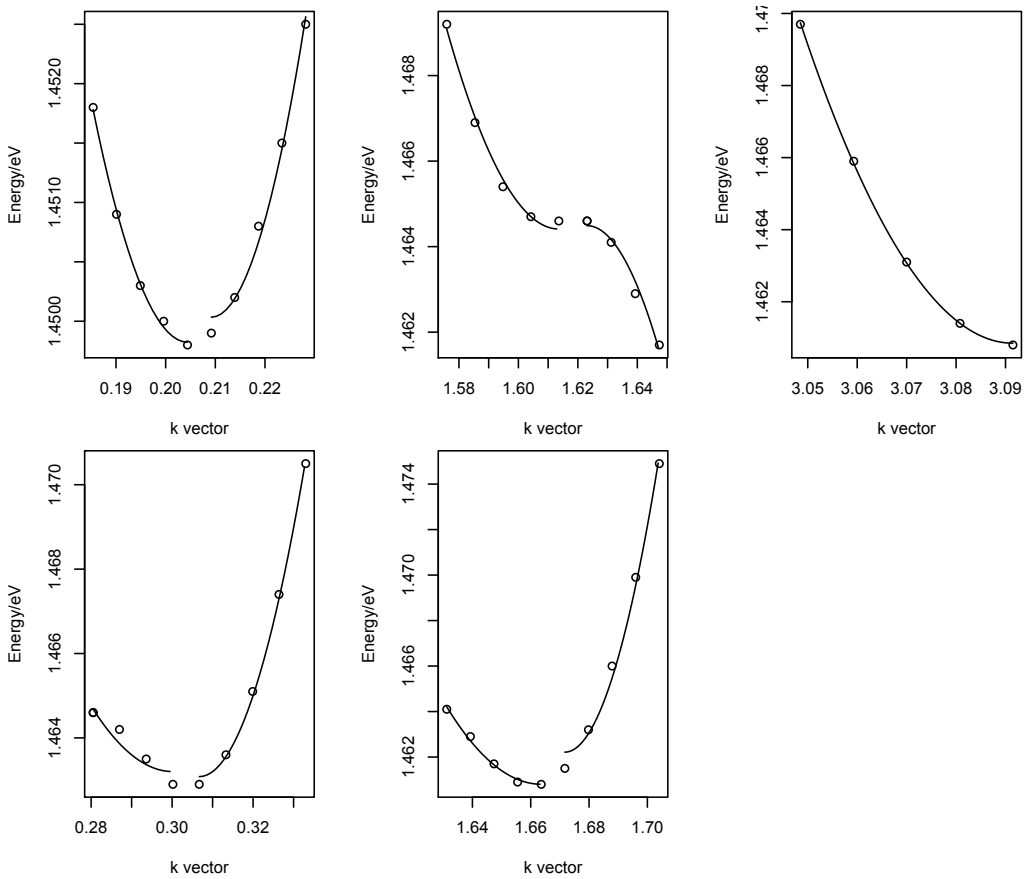

Figure S5: $MAPbCl_3$ CB1 near Γ point on the direction of Z-Γ (left half of top-left), Γ-X(right half of bottom-left), M-Γ (left half of top-mid), Γ-R (right half of bottom-left), R'-Γ (top-right) and its fitting for mass evaluation.

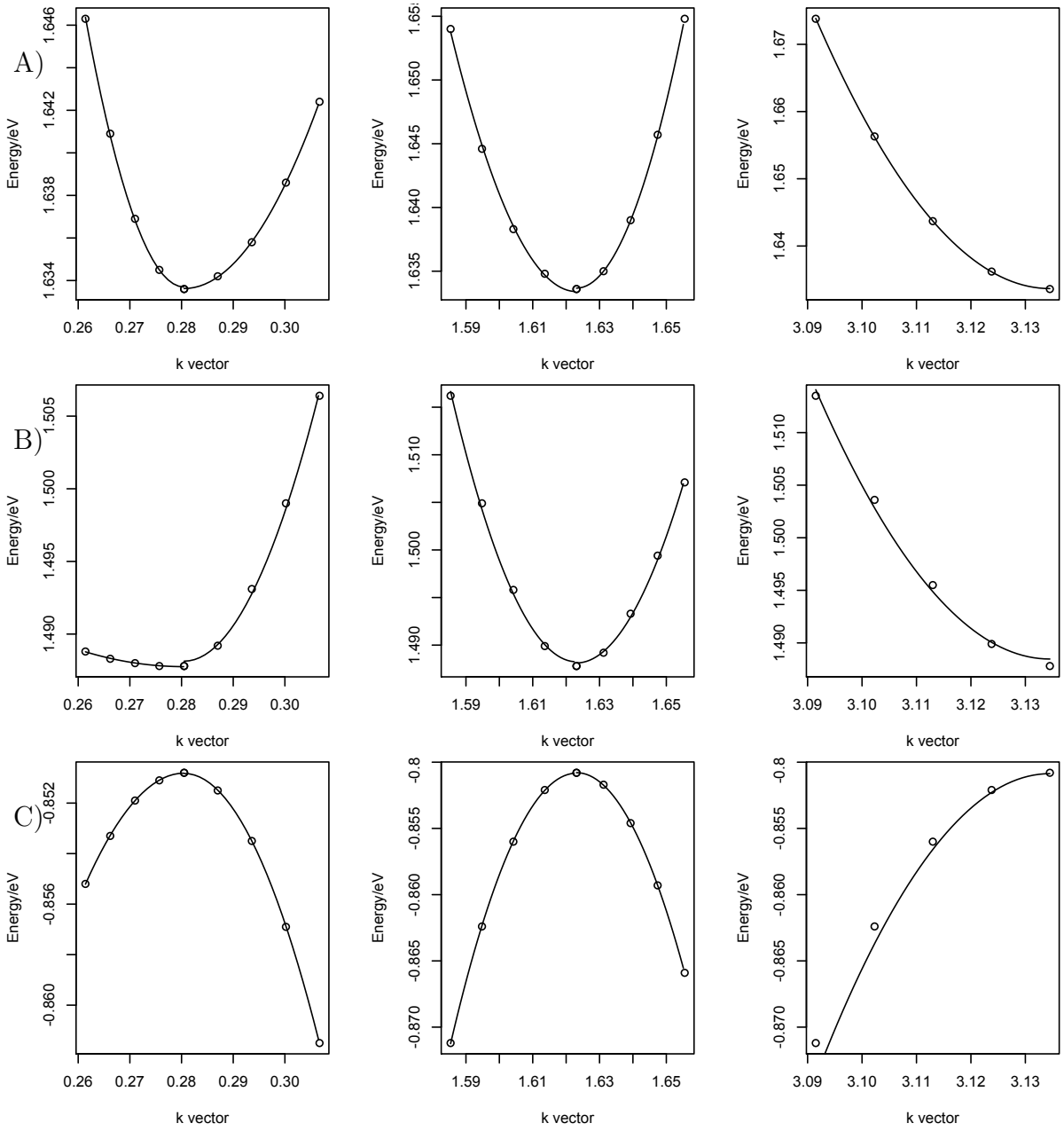

Figure S6: $MAPbCl_3$ A) CB2; B) CB1; and C) valence band near Γ point on the direction of Z-Γ (left half of left figure), Γ-X(right half of left figure), M-Γ (left half of middle figure), Γ-R(right half of middle figure), R'-Γ (right figure) and its fitting for mass evaluation.

Effective mass of $MAPbI_3$

Table S6: $MAPbI_3$effective masses and effective mass DOSs.

Bands	Z-Γ	Γ-X	Γ-R	Energy	g	M_{eff}	DOS of band	Total DOS	Product
CB3	0.08	0.13	0.13	0.86	1	0.11	8.90×10^{17}		
CB2	0.46	0.09	0.11	0.83	1	0.16	1.66×10^{18}	6.98×10^{18}	1.74×10^{37}
CB1	0.53	0.36	0.17	0.79	1	0.32	4.55×10^{18}		
VB	-0.23	-0.20	-0.21	-0.77	1	0.21	2.49×10^{18}	2.49×10^{18}	

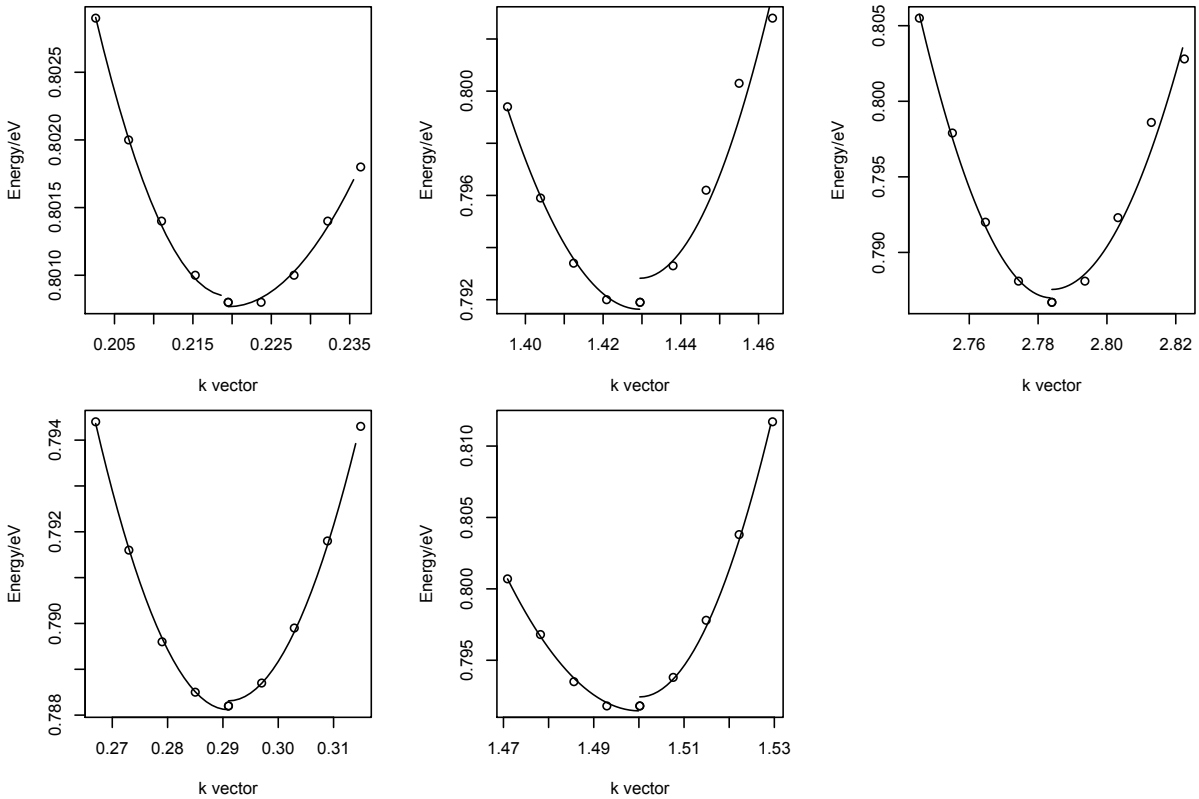

Figure S7: $MAPbI_3$ CB1 near Γ point on the direction of Z-Γ, Γ-X, M-Γ, Γ-R, R'-Γ and its fitting for mass evaluation.

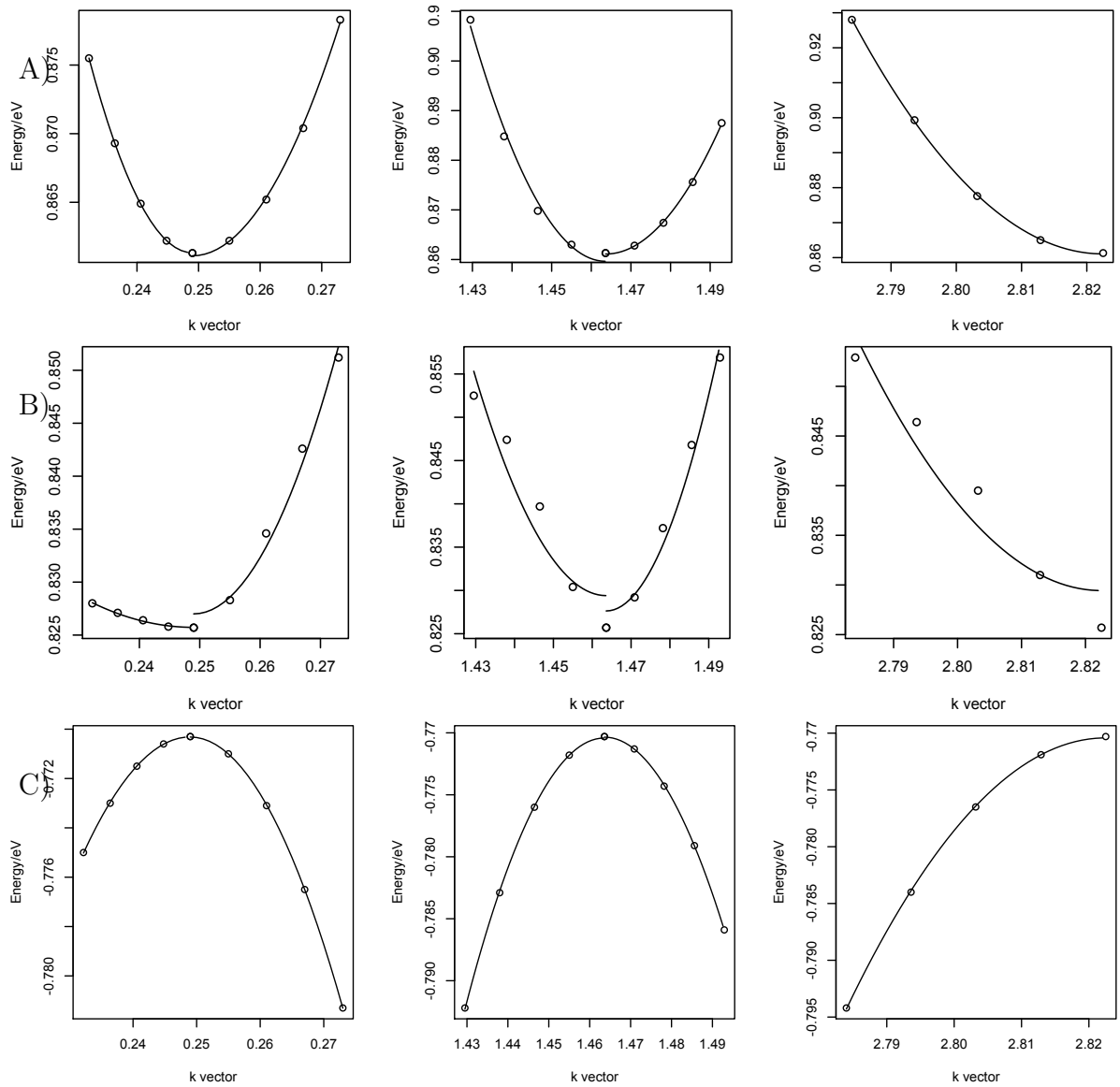

Figure S8: $MAPbI_3$ A) CB2; B) CB1; and C) valence band near Γ point on the direction of Z-Γ (left half of left figure), Γ-X(right half of left figure), M-Γ (left half of middle figure), Γ-R(right half of middle figure), R'-Γ (right figure) and its fitting for mass evaluation.

Effective mass of CdTe

Table S7: CdTe effective masses and effective mass DOSs.

Bands	Γ-X	M-Γ	Γ-R	g	M_{eff}	DOS of band	Total DOS	Product
CB	0.06	0.07	0.07	1	0.07	4.25×10^{17}	4.25×10^{17}	
VB1	-0.51	-2.68	-1.11	1	1.15	3.14×10^{19}		1.93×10^{37}
VB2	-0.51	-0.51	-1.11	1	0.66	1.37×10^{19}	4.54×10^{19}	
VB3	-0.06	-0.06	-0.06	1	0.06	3.86×10^{17}		

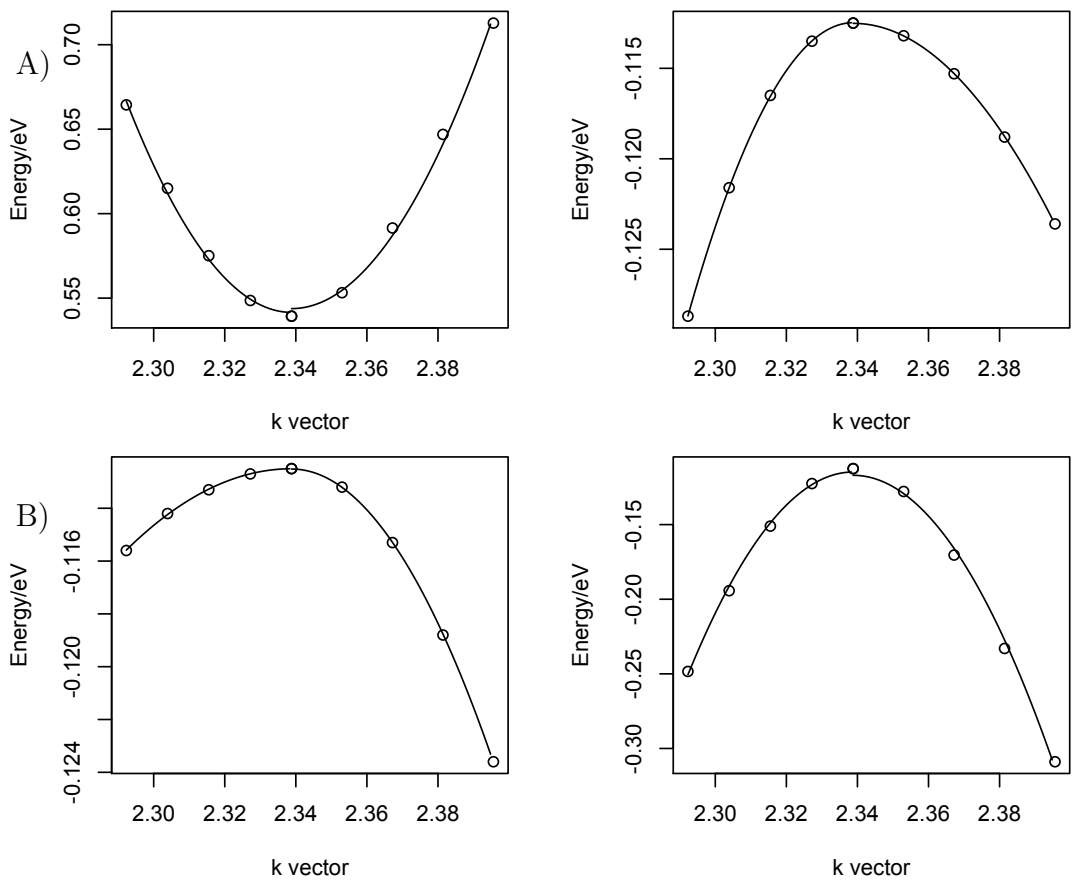

Figure S9: CdTe valence (top-left) and conduction bands near Γ point on the direction of M-Γ, Γ-R and its fitting for mass evaluation.

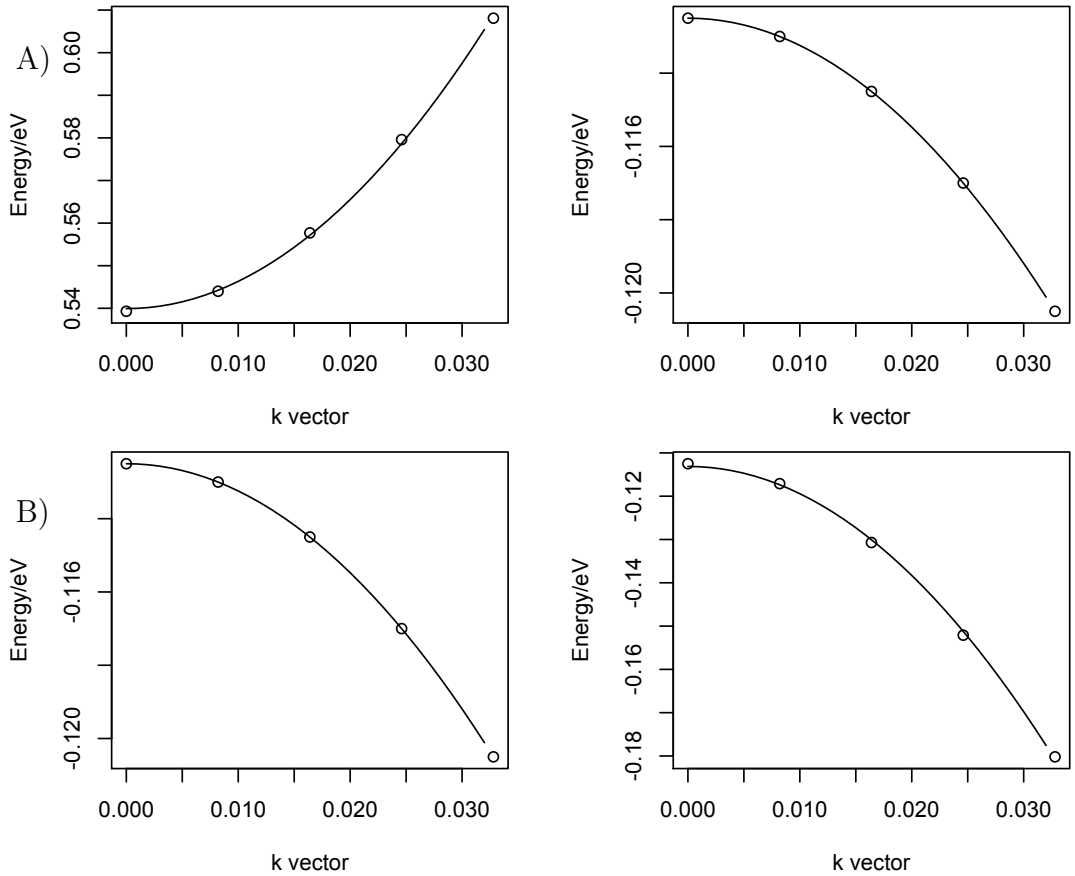

Figure S10: CdTe Valence and conduction bands near Γ point on the direction of Γ-X and its fitting for mass evaluation.

References

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