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Full Paper

Crossing points in the electronic band structure of vanadium oxide

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Abstract: The electronic band structures of several models of vanadium oxide are calculated. In the models 1-3, every vanadium atom is connected to 4 oxygen atoms and every oxygen atom is connected to 4 vanadium atoms. In model 1, a=b=c 2.3574 Å; in model 2, a= 4.7148 Å, b= 2.3574 Å and c= 2.3574 Å; and in model 3, a= 4.7148 Å, b= 2.3574 Å and c= 4.7148 Å. In the models 4-6, every vanadium atom is connected to 4 oxygen atoms and every oxygen atom is connected to 2 vanadium atoms. In model 4, a=b= 4.551 Å and c= 2.851 Å; in model 5, a=b=c= 3.468 Å; and in model 6, a=b=c= 3.171 Å. We have searched for a crossing point in the band structure of all the models. In model 1 there is a point at which five bands appear to meet but the gap is 7.3 meV. In model 2 there is a crossing point between G and F points and there is a point between F and Q with the gap ≈ 3.6608 meV. In model 3, the gap is very small, ~ 10^{-5} eV. In model 4, the gap is 5.25 meV. In model 5, the gap between Z and G points is 2.035 meV, and in model 6 the gap at Z point is 4.3175 meV. The crossing point in model 2 looks like one line is bent so that the supersymmetry is broken. When pseudopotentials are replaced by a full band calculation, the crossing point changes into a gap of 2.72 x 10^{-4} eV.

Keywords: vanadium oxide, band crossing points, supersymmetry

Introduction

Recently, it has been observed that there are crossing points in the band structure. The valence band appears as a cone with apex on top while the conduction band does with apex at the bottom. The apex point of the conduction band sits on top of the apex point of the valence band. If we take a point

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on the cone of the conduction band with energy E, then for the same wave vector, in the valence band there is a point with energy –E. When the magnitude of the energy E in the conduction band is equal to the magnitude of the energy –E in the valence band, there is supersymmetry; otherwise the supersymmetry is broken. In the theory of relativity, the energy of a particle of momentum p and mass m is given by $\pm (c^2p^2 + m^2c^4)^{1/2}$ where the magnitude of the energy with positive sign is exactly equal to that with negative sign. This is called the supersymmetry. In the Dirac equation, the negative energy states are associated with a particle of positive charge called the positron and the positive energy solutions are associated with the electron. The electron energy solutions found in the non-relativistic Schrödinger equation may be mapped to that of the Dirac equation. The two-energy solutions in $\pm (c^2p^2 + m^2c^4)^{1/2}$ never cross but it is possible to select a point in the middle of the two solutions which is named as the "Dirac point" [1, 2]. The geometric average of the two energies in which one is a constant and the other varies as n will vary as the square root of n. For zero mass, mc^2 term is zero and the c^2p^2 term varies linearly as a function of momentum. This linear dependence with both ± signs forms a crossing point called the "Dirac point" as shown in Figure 1.

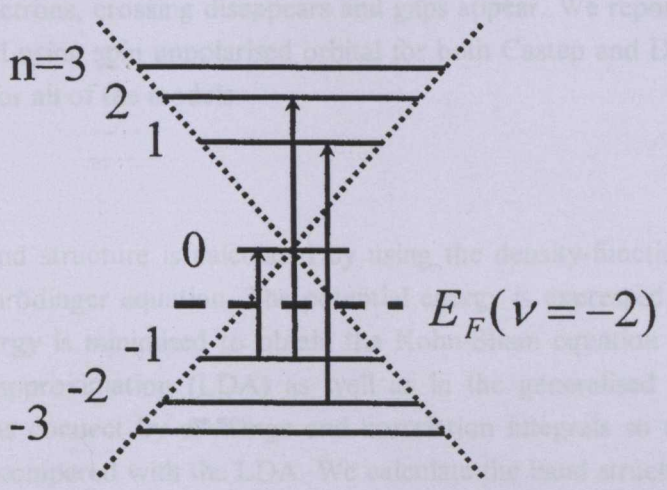

Figure 1. The crossing point of the two dash lines becomes a cone when visualised in three dimensions. The crossing point can be at the top of one cone and at the bottom of another cone and hence matches with the apex point. The position of Fermi energy can be fixed from an independent calculation [2].

The energy mc^2 in the Dirac equation is of the order of 0.5×10^6 eV, which is very large compared with the energies $\approx 10^{-3}$ eV found in the semiconductors. If there is a point in the centre of the conduction and valence bands it should be called the Schrödinger point. The object of the present study is to look for crossing points in the electron energy bands obtained from the solutions of the density-functional theory. In a calculation of band structure of a monolayer of carbon atoms, the crossing point with the supersymmetry was searched [3]. In a recent study of the crossing points and band bending in TiO_2/VO_2 nanostructures, semi-Dirac points have been discussed [4]. The compounds of vanadium show several different valencies. In VO_2, the valency of vanadium is 4. The VO_2 shows several phases as a function of temperature and pressure. For T > 340 K it has a pseudo R phase. For the pressure larger than 200 bar and temperature less than 340 K, the phase is called M_1, and for T < 340 K but larger than -0.0099 P + 340 K, where P is the pressure measured in units of bar, the phase is

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called M_2 [5]. There is a Peierls distortion so that the vanadium atoms occur in pairs [6]. The electronic configuration of vanadium is $3d^34s^2$. In the tetravalent position, it is $3d^1$. Hence, two atoms form a spin triplet. The experimental optical gap is 0.6 eV [7] but the calculated value is -0.04 eV [8]. Hence, it will be of interest to calculate the gap energy. The compounds $V_{2n}O_{5n-2}$ are known as Wadsley phase and V_nO_{2n-1} are called Magneli phase. It is clear that many phases with different valencies occur and there are phase transitions as a function of pressure. The Raman spectra of VO_2 show a phase transition at a pressure of 12 GPa. It has been shown that the metal-insulator transition and the electronic structure are correlated [9]. The M_1 phase of VO_2 is charge ordered [10]. There are a series of avalanches which depend on the particle size before the transition is completed [11]. A point-ion model has been described by Nakatsugawa and Iguchi [12]. The early ideas of the metal-insulator transition were given by Zylbersztejn and Mott [13].

In the present work, we have made six models of vanadium oxide. Out of these six models, three have vanadium valency equal to 2 and the remaining 3 have vanadium valency equal to 4. In all of the cases we optimise the structures and calculate the band stuctures to look for crossing points. We find a crossing point only when pseudopotentials are used in Castep programme. In the full calculation, taking into account all of the electrons, crossing disappears and gaps appear. We report all of the gaps found. The models are calculated using spin unpolarised orbital for both Castep and DMol3 programmes. We take the P1 space group for all of the models.

Materials and Methods

The electronic band structure is calculated by using the density-functional theory which is an approximation of the Schrödinger equation. The potential energy is expressed in the form of electron density and then the energy is minimised to obtain the Kohn-Sham equation [14, 15], which can be solved in local density approximation (LDA) as well as in the generalised gradient approximation (GGA). The actual atoms connect by exchange and correlation integrals so the linear GGA is quite approximate but may be compared with the LDA. We calculate the band structure by using the DMol3 (all electrons) as well as the Castep (pseudopotentials) programmes [16]. We present the results of the calculation of the gap energy in both approximations. All of the results are obtained in LDA and unpolarised orbitals are used. Both the Castep and the DMol3 were kindly provided by Accelrys Software Inc, San Diego, CA. The geometry and the unit cell sizes (a, b and c) are calculated by minimising the energy of the Schrödinger equation for each model.

Results and Discussion

Models of vanadium oxide

Model 1: VO. In this model, V atom is coordinated with 4 oxygen atoms and every oxygen atom is coordinated with 4 vanadium atoms. The V-O distance is 1.667Å and a=b=c=2.3574Å. The coordinates of k points are G (0, 0, 0), F (0, 0.5, 0), Q (0, 0.5, 0.5) and Z (0, 0, 0.5). The model is shown in Figure 2 and the calculated band structure along with the density of states (DOS) is shown in Figure 3, which

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also identifies the various zone points. The Fermi energy, the binding energy and the gaps at the k points are given in Table 1.

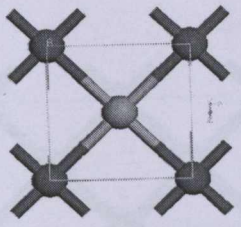

Figure 2. Model 1: The central V atom is connected to 4 oxygen atoms.

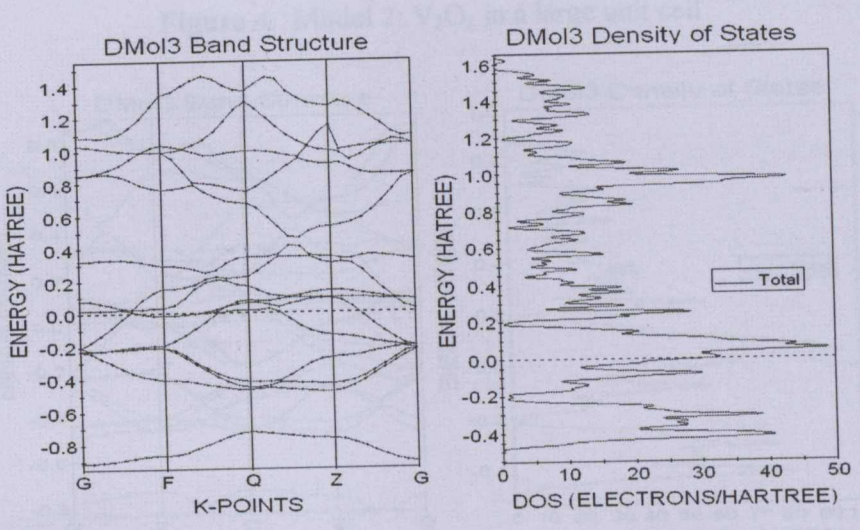

Figure 3. The band structure and the DOS of model 1

Table 1. The Fermi energy, the binding energy and the energy gap at various k points

		Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
Fermi energy (eV)		7.2234	7.0312	7.1722	6.6447	6.9399	6.8908
Bind. energy (eV)		10.931	21.8223	43.6524	19.8832	20.4224	17.4416
Energy gap (eV)	G	6.1907	4.2791	0.5851	0.9252	0.8844	0.1361
	F	1.1565	0.8028	0.7891	0.7551	1.2586	1.5579
	Q	11.7012	5.4152	0.2177, 1.1905	1.83	2.5035	1.4558
	Z	6.1907	2.4899	2.9729	0.1905, 2.0953	0.9456	1.1837

Model 2: V_2O_2. In this model every vanadium atom is coordinated to 4 oxygen atoms and every oxygen atom is also coordinated to 4 vanadium atoms. The layering of atoms is such that b=c=2.3574Å

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and a=4.7148Å. Thus, the cell is much bigger than in model 1. The V-O distance is 1.667Å. The model is shown in Figure 4 and the calculated band structure and the DOS are shown in Figure 5. The gap energies at the k-points are given in Table 1.

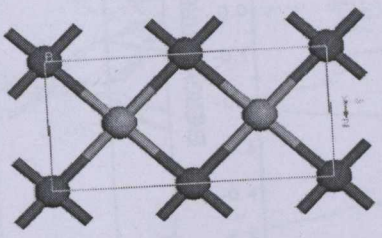

Figure 4. Model 2: V_2O_2 in a large unit cell

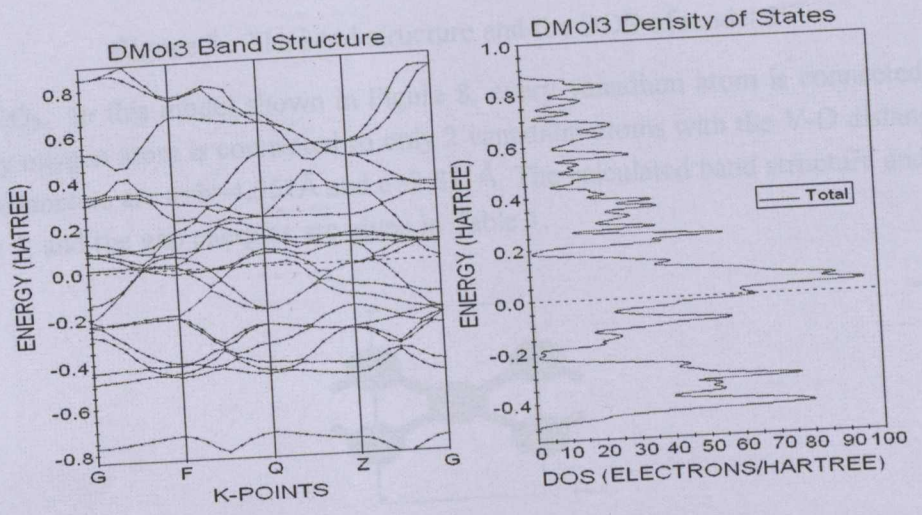

Figure 5. The band structure and the DOS of model 2

Model 3: V_2O_2. In this model a=c=4.7148Å and b=2.3574Å. The binding energy in this model is twice that of model 2. The model is shown in Figure 6 and the band structure along with the DOS is given in Figure 7. The gap energies are given in Table 1. The gap at the G point is in agreement with the experimental value [6]. The calculated value of 0.58 eV is to be compared with the experimental value of 0.6 eV.

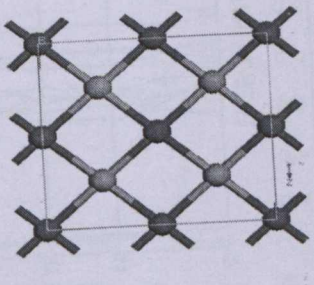

Figure 6. Model 3: Another model of V_2O_2

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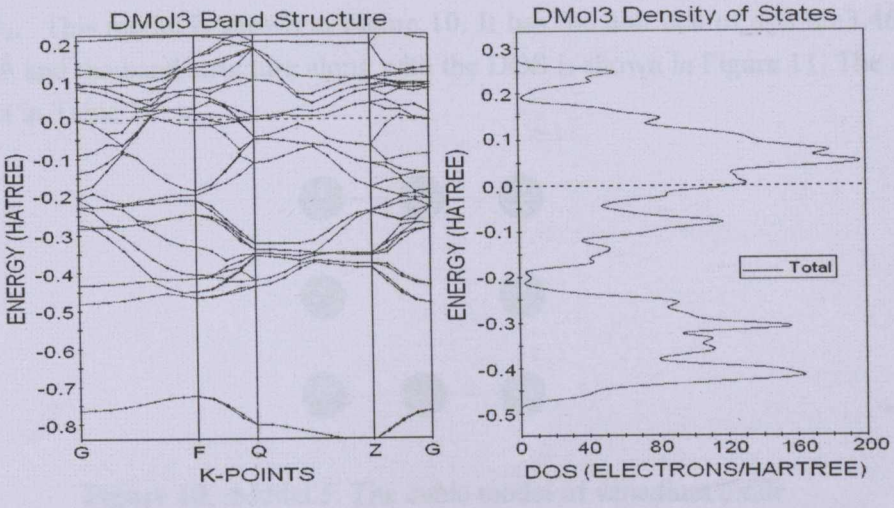

Figure 7. The band structure and the DOS of model 3

Model 4: VO_2. In this model shown in Figure 8, every vanadium atom is connected to 4 oxygen atoms but every oxygen atom is connected to only 2 vanadium atoms with the V-O distance of 1.895Å. The unit cell parameters are a=b=4.551Å and c=2.851Å. The calculated band structure and the DOS are given in Figure 9, and the gap energies are given in Table 1.

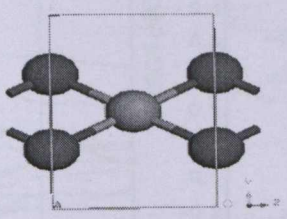

Figure 8. Model 4: One vanadium atom is connected to 4 oxygen atoms and one oxygen atom is connected to 2 vanadium atoms.

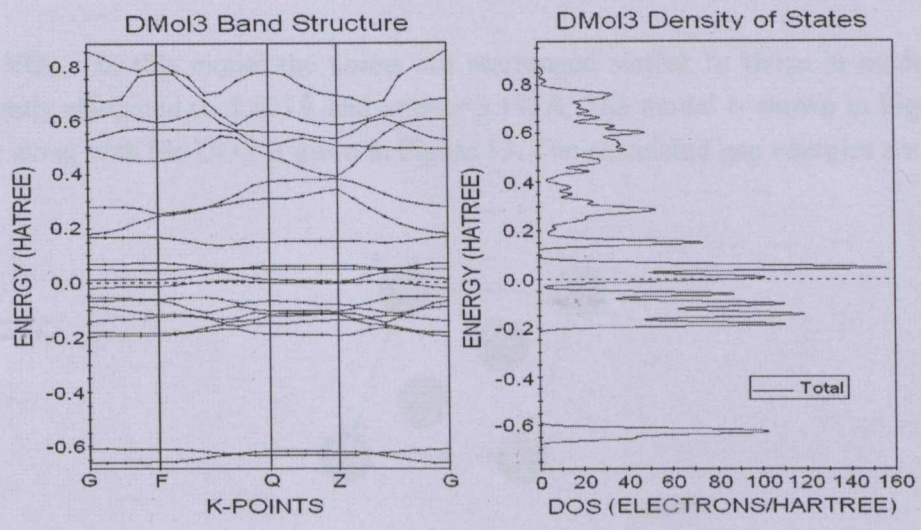

Figure 9. The band structure and the DOS of model 4

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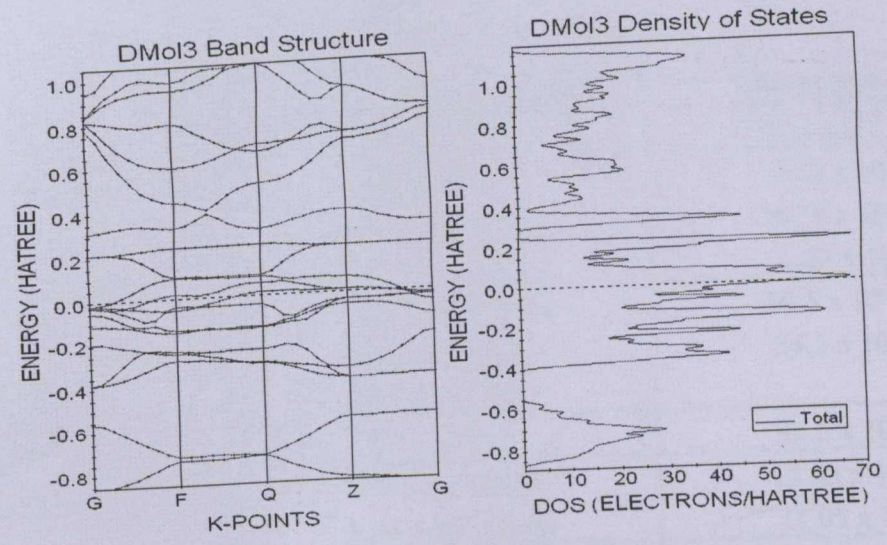

Figure 13. The band structure and the DOS of model 6

Crossing points

When we magnify all the band structures to search for crossing points, we find that all crossing points actually open a gap except in model 2 in Castep (pseudopotentials). When the program takes into account all the orbitals, these crossings also change into a small gap. These small gaps are shown in Table 2. It can be observed that Castep gives zero value for the gap, whereas DMol3 gives a small value, 2.72×10^{-4} eV, in model 2 in between G and F points. This is due to the interactions between electrons. Thus, the pseudopotential method does not see the small gaps at some places which can be seen when all of the electrons are considered properly.

Supersymmetry

In Figure 14, the crossing point obtained from the Castep calculation of model 2 is shown. In fact when all of the electrons are taken into account, this crossing point opens up a gap of about 2.72×10^{-4} eV. If we look at the cross carefully we find that it is not a cross of two lines but a confluence point of four lines.

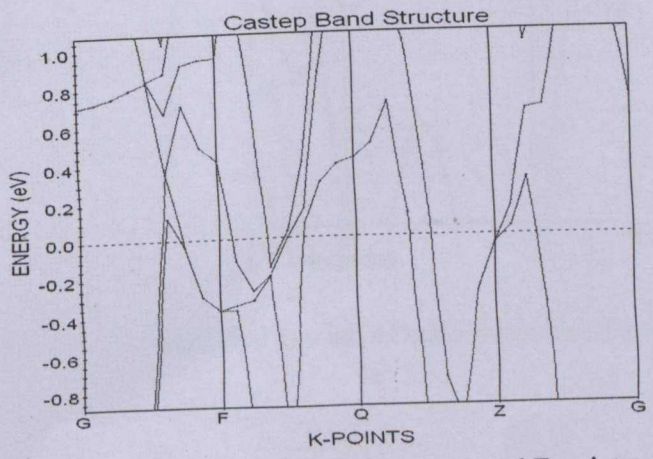

Figure 14. Crossing point in the space between G and F points at about 0.3 eV

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Table 2. Small energy gaps between two k points or at a k point in eV

Model	Castep (pseudopotentials)	DMol3 (all electrons)
Model 1	7.3×10^{-3} (G-F)	17.2×10^{-2} (G-F)
Model 2	0.00 (G-F) 3.66×10^{-3} (F-Q)	2.72×10^{-4} (G-F) 18.12×10^{-3} (F-Q) 1.53×10^{-3} (F-Q)
Model 3	7.35×10^{-3} (G-F) 2.88×10^{-5} (Q) 6.25×10^{-5} (Q)	10.3×10^{-3} (G-F) 34.5×10^{-3} (F-Q)
Model 4	5.25×10^{-3} (F)	32.5×10^{-3} (F-Q)
Model 5	9.48×10^{-3} (G-F) 2.04×10^{-3} (Z-G)	13.03×10^{-3} (G-F) 11.05×10^{-3} (G-F)
Model 6	12.43×10^{-3} (Z) 4.32×10^{-3} (Z) 10.43×10^{-3} (Z-G) 10.23×10^{-3} (Z-G) 4.38×10^{-3} (Z-G)	32.27×10^{-3} (G-F) 3.62×10^{-4} (Z-G) 9.36×10^{-3} (Z-G) 11.43×10^{-3} (Z)

When we draw a horizontal line and look for the positive solutions above the line and compare them with those below the horizontal line, the supersymmetry is not found. The expanded version of the Castep band structure of model 3 shown in Figure 15 also shows gaps between G and F points which in DMol3 show gaps.

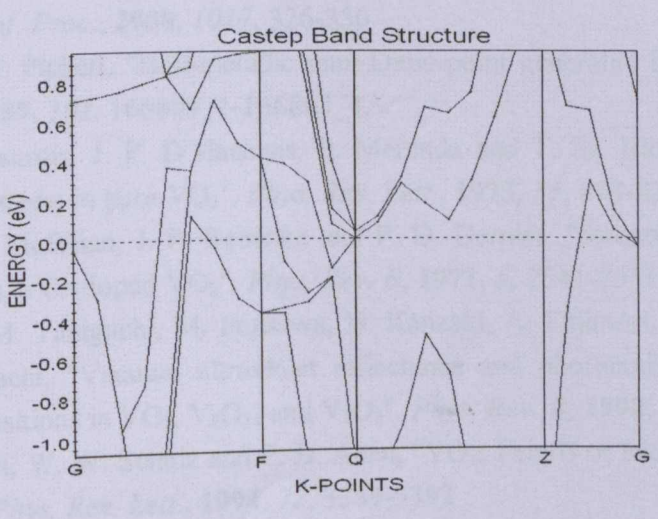

Figure 15. The expanded version of band structure of model 3

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Conclusions

We have studied 6 different models of vanadium oxide and have calculated the gaps in all of the cases. In models 1-3, the valency of vanadium is two so that we see the alignment of V^{2+} ions, whereas in models 4-6, vanadium has a valency of 4, thus showing the ordering of V^{4+} ions. We have searched for the crossing points by using two valencies and six models but discovered "confluence points." The crossing may be called the "Dirac point." However, our calculation is non-relativistic and hence "Schrödinger point" is a more appropriate terminology for the crossing point.

Acknowledgements

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