含磷酸根環氧樹脂塗料對金屬表面黏著力之量子力學計算

期末報告

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中油計畫的結案報告

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中文摘要

（目的）
本研究計畫，就是希望從精確量子力學計算之方法出發，試圖從原子尺度的觀點，來了解含磷酸根環氧樹脂中其高分子鍊上的各重要單元在吸附時所扮演的角色。其中的一個重要應用，即子計畫二中提到的，設計出對金屬表面吸附力強的含磷酸環氧樹脂塗料以對抗腐蝕。在這一個問題上，塗料對表面的附著力是是決定塗料品質的最重要因素之一。

（方法）
爲了忠實呈現出表現出"金屬"及"表面"的量子效應，採用週期性邊界條件以消除邊緣效應，並且以 k 點採樣表現出金屬費米面的特性。至於高分子鍊上的各種官能基，則以分子片段模擬之以進行吸附的量子力學計算。固體或表面等延伸系統則是由能帶結構來決定，與分子由能階表現其量子狀態不同。能帶結構提供科學家了解及預測固體及表面性質的重要依據，但由於晶體或表面之複雜，能帶結構若不經過適當工具程式的分析或解讀，很難從其中獲取有用的資訊。解讀能帶結構的良好方法之一是態密度對能量的分佈圖。我們對整體結構中的局部分子或原子片段有興趣，則有兩種選擇，採用空間切割法或是軌道投影法，兩者都可以幫助我們在來自塊狀固體及表面之延伸的電子態中，定量地求得所指定的個別部位對全體量子態所造成的貢獻。

（結果）
分子片段吸附在鋁表面的鍵能、量子態密度及部分態密度、軌域電荷分佈圖。其中磷酸根的吸附能/鍵能的確是最強的，也是離子性最高的。鍵能大小的排列依序是：磷酸根、R-[C]-R、R-[C]-O-R、R-C[O]-R。（只其 [ ] 中之原子表示直接接到金屬表面者。）至於鐵表面之吸附，爲了簡化計算，我們採用只有吸附位置有鐵，而其他原子則仍是由鋁構成的簡化模式。如此仍然得到磷酸根是有最強鍵能的趨勢。除了鍵能之外，各組計算都有部分態密度及軌域密度圖以供後續的分

英文摘要

Abstract

The purpose of this project is to us accurate Quantum Mechanics computational method, which is capable of study a system at atomic level, to understand the roles played by various unit on the polymer chain of PO4 containing epoxy-resin. One of the important application, as indicated in sub project No.2, is to design such epoxy-resin which has strong cohesion to the metalic surface so that it is be used to resist corrosion. On this issue, the cohesiveness of the coating to the surface is one of the most important measure for the quality of the coating material.

In order to faithfully describe the quantum effect of "metal and "surface", periodic boundary condition is used to eliminate the edge effect, and k-point sampling carried out to have a good representation of fermi surface of metal. As for the various functional group on the polymer chain, molecular fragment is used to mimic them to perform the quantum simulation of adsorption. It is well known that the solid and surface quantum states are characterised by the band structure, not just by the energy levels which determined the molecules. Band structure provides a important source of information for scientists to understand and predict the properties of crystalline solids and surfaces. However, due to the complication of crystals or surfaces, it will be very difficult to extra useful information just right from band structure without help use analysis methods and tools. A very way to do this is to use the Density of State analysis. If we are interested in some local atomic or molecular fragment in the overall structure, we may choose either space division method for orbital projection method. Both will allow one to quantitatively obtain the partial contribution of selected components to the entire quantum states of extended systems of solid and surface.

Our results include the binding energies, density of states and partial density of states, orbital density of high-lighted states of various molecular fragments adsorb on Aluminium surface. We found that the phosphate has the strongest bond, and highest on ionic character. The order of the binding energy of species is: PO4, R-[C]-R, R-[C]-O-R, R-C[O]-R. (We use [ ] to denote the atomic species that have direct connection to the surface.) As for the case of iron metallic surface, to simplify the calculation, we have adapted the models that only the adsorption site has Fe atom, and use Al as replacement on other sites that has longer distance away from the molecule. Given the model is simplified, PO4 still top the strength of binding compared with

other fragments. In addition to the binding energies, PDOS and orbital density plots are collected for further investigation. From the comparison between cases before and after adsorption, the change of quantum states indeed directly corresponds to the formation of the chemical bond. We have observed two kinds of mechanism (bonding) from the plots of electron density plots, namely covalent adsorption and ionic adsorption, which depends on the type of atoms that the metallic surfaces are consist of.

We conclude that PO4 has indeed a stronger chemical bond compared with other functional units on the epoxy-resin polymer chain. The change of quantum states is different for the cases with different functional groups, thus provide information for investigation of mechanism of the bonding strength. More over, the orbital density plots offer direct proof of the bonds in quantum states, and we can therefore identify the dominating quantum states for cohesion. This is extremely useful for predicting the behaviour under the similar adsorption condition.

報告正文

緒論

塗料化學是一門與民生息息相關的領域，舉凡器物表面之保護，不管是阻隔光、電、滲透等物理現象或是氧化、腐蝕等化學過程，塗料在今曰文明中可說是不可或缺。塗料區隔了兩個物理狀態或是物質組成迥然不同的世界，而創造了人類在器物與工具利用上的無限可能性。既然它如此重要，因此希望塗料強固耐用的預期是必然的。高分子技術的應用，使得塗料材質本身設計變爲可能，而能發展出在機械性或化學特性上能因應各種功能上需求的高分子塗料。在這其中的一個重要應用，即子計畫二中提到的，設計出對金屬表面吸附力強的含磷酸環氧樹脂塗料以對抗腐蝕。在這一個問題上，塗料對表面的附著力是是決定塗料品質的最重要因素之一。

在實驗上已經知道，當使用含有磷酸根的高分子環氧樹脂作爲塗料時的，它對鐵的附著力可以被加強。但是同樣的塗料在其他種類的金屬表面何如鋁、鋅等卻有大不相同的附著力。如果我們可以了解其機制，則必將對子計畫二之抗腐蝕塗料的發展產生極有利的影響。

本研究計畫，就是希望從精確量子力學計算之方法出發，試圖從原子尺度的觀點，來了解含磷酸根環氧樹脂中其高分子鍊上的各重要單元在吸附時所扮演的角色。因爲從微觀的角度來推想，塗料在光滑金屬表面之附著程度的強弱，必然是取決於塗料分子和金屬表面所發生的交互作用，然而高分子上的分子結構是各式各樣的都有，自然當它吸附於金屬表面之上時，交互作用也就各有其不同的貢獻。在本研究計劃中，我們最想要了解的，就是爲什麼環氧樹脂這樣的高分子在含有磷酸根時，其與鐵的結合力會變強，在高分子鍊兩端之磷酸根和在高分子鍊上的磷酸根可能以單配位與金屬原子發生鍵結，也可能以多芽鉗狀的方式去與抓住金屬原子。其他尙有高分子鍊上的 COH 也可能因爲其極性的關係而與金屬表面有作用。經由量子力學計算，如果我們知道那一種機制有較強的鍵能，則可以確認高分子鍊兩端的磷酸根是否如預期良好附著力的主要貢獻，並且也可以得知高分子鍊上的 P=O 在整個材料的黏著力上扮演怎樣的角色。

由上述的說明可以知道，分子構形、鍵能、電子分佈、原子排列等微觀尺度的物理量，是用來了解黏著力強弱機制的關鍵。然而，與塗料與金屬表面之間附著力的研究，仍是一個具有挑戰性的課題。首先，從實驗資料的來源來看，磷酸根與

金屬表面交互作用之實驗研究並不常見，原因是大多數金屬表面化學或物理吸附的研究其對象都是如 CO、CO2、NO、等小分子，如此才能讓表面分析的實驗較爲可行，然而磷酸根 PO 甚少存在於簡單的氣體分子的組成之中，因此也就不像 CO 與 NO 那樣，在與金屬表面之鍵結上有充足實驗數據。其次，從理論計算的觀點，由於金屬表面與高分子在幾何上的本質都是延伸性的，因此極不適合以分子團的方式來模擬，這也就是說，化學家常用的量子化學程式在此並不合用。更重要的是，我們所探討的問題涉及金屬的表面，它是能帶的問題，而非只是孤立金屬原子或原子團只由能階來描述即可，就其材料的本質來看，必定要用固態物理所擅長的能帶電子結構方法。

本計畫申請人過去多進行固態物理及表面物理的電子結構計算 [Ref.1,2,3]，也曾經參與對於過渡金屬表面與分子的交互作用 [Ref.4,5,6] 以及共軛高分子的力學特性 [Ref.7] 等研究。在本計畫中，金屬表面與高分子共存，並且磷酸根官能基將會與金屬表面產主交互作用。於是我們便可借助過去在處理分子團與週期性系統交互作用的技術，來進行本計畫中的一系列計算。如此一來，高分子鍊也可以模擬成週期性無限延伸的長鍊，而不必因就於傳統量子化學之分子團計算必須取一個有限大小的限制。總之，固態物理的能帶結構方法，使計算可以忠實地模擬金屬表面，又完全不會有非週期性方法中所必然會伴隨的不真實的邊緣效應。這也就是爲什麼，我們在固態表面物理能帶計算上的技術及經驗，可以成爲進行此一計算工作之優勢。

從研究方法的設計與規畫來看，應用科技研究的成果及其獲得的經驗與方法，如果不能有效地轉移給業界，則成效必然是大打折扣。本研究計劃中的量子計算是絕對不同於一般純學術研究的曲高和寡型計算，具有技術轉的價值和條件。在價值方面，此程式 CASTEP 是一個知名於學術界的程式，具有多種先進的設計以便精確地解出複雜系統的電子結構及所有相關物理量，並且核心發展小組仍不斷地引入最新的學理以便提昇其效能，讓中小型工作站也能夠進行高品質的運算以解決極複雜的問題。自 1991 年被開始使用至今，在知名期刊上已有百篇以上文獻報告各式的應用，可謂相當成熟穩定的技術。在條件方面，CASTEP 的商業化版本 Cerius 2・CASTEP 由全世界規模最大的專業科學計算軟體公司 Molecular Simulation Inc.（MSI）發行，結合了當今最優良的 3D 圖界面技術，再複雜的電子雲分佈與化學鍵連結都一覽無遺。特別爲了容易操作而設計的使用者界面，更使得執行複雜的量子運算有趣如動畫遊戲。尤其是此程式有大型的軟體公司發行與支援，將來計劃完成且技術轉移之後，中油也不必擔心軟體的支援昇級以及人員的訓練等問題。

計畫申請人正好也是 CASTEP 程式發展小組的一員，且已經有七年使用及開發 CASEP 程式之經驗。個人在研究工作方面的重心即是發展、應用、及推廣此一量子力學計算，目前更執行國科會國家高速電腦中心之中英國際合作專案計畫，參與程式新功能的開發以及定期在高速電腦中心舉辦講習會（兩個月一次），以協助來自各界之新使用者利用 CASTEP 來進行諸如半導體特性、金屬表面結構、觸媒機制、非線性光學吸收等應用材料研究。我們因此有把握在本計畫完成之後，不但能將研究的結果提供中油參考，並且我們保證對本計畫過程中使用之方法、策略等全盤的規劃框架與實際進行之步驟及模式，透過結案報告的整理以及人員訓練的方式，協助中油或中油指定之研發單位，使其具備相同的研究能力，以利其在高分子科技上進行更深入的研究。

本研究案之預期成效爲：(1) 了解機制：經由精確的量子計算，了解磷酸根在高分子中與金屬表面交互作用的機制。(2) 協助設計：對含磷酸根環氧樹脂對金屬表面黏著力機制的了解，將有助於設計更優良的防蝕塗料（支援子計畫二）。(3) 建立方法：一旦本研究計畫能達成目標，則使用的方法與策略可謂完全確立，即可進一步被當作未來相關研究的標準程序。(4) 培植人才：參與本計畫的專任及兼任研究助理，都將受到固態及表面量子力學計算之訓練，未來針對類型相似的個案研究將更能得心應手。(5) 轉移技術：透過結案報告的整理以及研討會的舉辦，在本計畫中所累積的經驗將可以爲中國石油公司所使用。

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詳細內容

研究方法

本研究計畫的基本精神，就是要使用一系列電腦模擬的計算工具，以逐步漸進的方面，來將含磷酸根環氧樹脂高分子對金屬表面之化學吸附效應加以精確地計算。並且將所建立的研究方法與經驗轉移至中油的研發部門，因此我們所選用的一系列配套的計算工具，也特別重視其業界的標準性、可靠度，以及軟體的可取得性。如此可以確保將來技術轉移及人員訓練之可行性。

基於以上考量，我們選擇了 MSI 公司的 Cerius2 計算環境來進行本研究。MSI 爲當今全球最大的科學軟體公司，其主力產品 Cerius2 包含了數十個研究材料科學與生命科學之軟體，這些模擬工具全部整合在一個高效能的 Open GL 三度空間繪圖介面之下，配合其極易於使用的分子建構工具，它可使電腦模擬的研究工作從開始建造分子與固體、表面結構，進而進行不同精確程度的模擬，直到最後的電子雲密度作立體圖示及材料的其他物理特性分析，都在一個高度整合的環境下達成。以下將列出本研究計畫中所要使用的軟體工具，並作簡介。

（一）三度空間分子建構工具

Cerius2 中的各種 Builder 提供了建立三度空間分子結構的一個快速而有效的一方法。它提供選取、取代、抓取、剪貼、化學鍵之連接與編輯等方便的功能，簡化了我們建立高分子長鍊的複雜度（因爲我們可以由鍊上基本的有機物單元，開始建造，再把分子團用 Crystal Builder 連成具週期性的高分子鍊）。一旦完成了整條長鍊，我們還能依照近似程度之不同，截下不同的官能基單元來進行獨立的吸附計算，而鍊上延伸出去之其他官能基對吸附產生什麼樣的協同效應，也可以藉著以所探討的分子單元爲中心，向外包含更多的分子單元來達成。

（二）力場模擬工具

開放式力場是 Cerius2 用來作初步結構最佳化的模組，它是基於擬合實驗數據資料庫來定義各種化學元素的原子之間應該有的交互作用，它本身因此具有在原子尺度下進行電腦模擬的能力。但由於力場模擬方法並不處理量子問題，因此只

對化學特性與結構單純的元素有較高的準確度，對其他則不然，也因此力場方法僅適用於初步的最佳化。換一個角度來說，正由於其不求解量子問題，力場工具往往能夠在使用小型單 CPU 工作站的有限計算資源下，完成結構的最佳化。

（三）CASTEP 量子力學材料計算工具

CASTEP 程式是 Cerius2 環境中的旗艦級軟體，它是由以英國劍橋大學爲核心的小組最先開放發展的，也因此得名，現在則有一個由數個知名研究群所構成的國際團隊共同開發 CASTEP 的新功能，本案立持人所屬的淡江亦爲發展團隊者之一員，因此每每能使用到 CASTEP 中最新的技術。 CASTEP 一開始即被設計成一個全方位的量子力學材料計算軟體，它是基於甫獲 1998 年諾貝爾化學獎的密度泛函理論來處理多電子的量子現象，以平面波作基底以避免不同基底的選擇所造成之誤差，並且使用贋勢（Pseudopotential）來代表真實的元素原子，使得材料的量子問題只需要處理價電子的效應而對較不參與化學反應內層作合理的近似。在其優良的設計下能使大尺度的電子結構計算獲得較高的效率。從原子分子到具周期性的固態、表面結構之量子模擬，以致於同時存在分子與週期性金屬表面的化學吸附，都可以在同一個程式架構之下進行相同理論參數，且相同近似條件下的計算，如此一來，所獲得的相關計算結果完全可以相減和比較。

（四）原子軌域投影分析工具

以全套量子計算來求得系統整體的波函數、電子雲分佈及相關物理量與化學性質，是本研究案要達成精確吸附模擬所需要使用的方法。但正由於如此，所解得的結果是來自所有處原子全體效應的總和，並不直接反映出各部份的貢獻及其重要性。這原本正是全套量子力學方法在精確性上具有優勢的保證，無可避免地在分析上造成不便。由本研究群配合 CASTEP 程式所自行研發的原子軌域投影工具程式，能在完成 CASTEP 計算後所產生之總的態密度下，分析出各原子在這些總量子態裏定量上的貢獻。如此一來，任何我們所關心的某一特定局部結構對系統總體的貢獻，以及其主要在什麼樣的能量範圍內貢獻，便能夠在以原子軌域爲基本單位的解析度被分析出來，達到我們要從一個整體的量子力學計算裏，抽離出局部之貢獻的目的。

（五）電子雲及鍵結分析工具

電子雲分佈在任何的量子力學計算都是重要而可提供大量、甚至關鍵性資訊的結果。其本身代表電子在空間中被發現的機率大小，而鍵結的位置及強度也可以從電子雲分佈的結果來加以分析。Cerius2 模擬環境已經整合了優越的體積視覺處理（Volumatic Visualisation)，能在三度空間以等高線及等高面表達電子雲分佈的特性。至於鍵能本身，則在 CASTEP 計算中已經有系統的總能量可得到，將有分子吸附之系統總能減去未吸附表面及獨立分子的總能和，即是因吸附所產生之化學鍵的鍵能。

研究資源

人力資源介紹：

碩士班兼任研究助理兩名

主要計算資源介紹：

（第一類）我們在計畫進行的初期，依照原先的計算資源規劃，使用本已有之 SGI 之 Power Challenge 高速平行工作站，該工作站總共搭載六個 CPU，本研究案執行過程中經常性能使用到 4 顆 CPU 左右。初期我們亦使用了國家高速電腦中心的帳號，但數量不大，僅用於初步測試。

（第二類）研究的後期經歷九二一大地震及本校科學館大樓大樓整修，斷電頻繁，諸多因素直接或間接影響對外網路連線不良。因此後期之計算則以本研究群在淡江大學材料模擬實驗室建置之個人電腦叢集來進行。本研究群使用個人電腦叢集已有兩年，由於是上一代的處理器，運算速度本身較慢，但由於處理器個數眾多，在此次計畫的計算上扮演了相當吃重的角色。我們鑑於叢集運算之高效能與價格比，已在下一年度計畫申請中提出昇級此一叢集之規劃，以便負載本計畫在下一年度一更深入及更繁重的計算。

（第三類）另外在圖形方面，使用 SGI O2 R5000 180MHz 來進行 3D 視覺化處理及繪圖的工作，該工作站價格內含 196 MB 之記憶體，三十萬

主要軟體工具 CASTEP 介紹：

計算理論：密度泛函理論

在諸多能描述多電子體系的量子力學方法裏，只有密度泛函理論最適合處理伴隨有化學鍵生成與斷裂的材料科學問題。這是因爲要處理這樣的問題，我們既需要一個能計算大尺度（至少 10 埃立方）範圍的量子力學方法，而此一方法對於電

一個能計算大尺度（至少 10 埃立方）範圍的量子力學方法，而此一方法對於電子結構與鍵能的預測又還要能夠達到一定的精準程度，這就非要密度泛函理論不可。一這也就是我們選擇使用 CASTEP 這一個基於量子力學材料計算程式的原因。

（一） CASTEP 簡介

所謂 CASTEP，是 CAmbridge Serial Total Energy Package，的縮寫。它是一個解量子力學問題的程式，具體地說，凡給定一初始的原子排列，CASTEP 能解出了此系統最穩定時的（基態）電子的分佈、系統的總能量、以及各原子的受力。由於量子力學足以精確地描述原子間的交互作用，CASTEP 便能根據此一受力的情形來移動原子，進行分子動力學的模擬。因此，CASTEP 這個計算工具結合了量子力學和分子動力學這兩種基礎理論，因此對於因爲在原子尺度發生了變化，而造成的物理或化學現象，具有極佳的預測能力。

CASTEP 的主要特長，是在於能用合理的計算量來進行大尺度、大規模的電子結構計算。傳統量子化學雖然能做非常精確的電子結構計算，但由於它理論與運算法本身的特性，使得其運算所需的時間，隨著所探討對象的大小呈高次方正比。以 N 的五次方爲例，把計算的系統僅僅擴張成兩倍大的代價，是三十二倍的計算時間。這樣的計算瓶頸大大地限制了使用該方法來進行固體、表面等與材料應用關係較直接密切的研究。

CASTEP 則是從傳統固態物理的角度出發，以較大的、或有週期性延伸的系統爲其主要的計算與模擬對象。它所採行的理論基礎以及所取的近似條件，尤其是演算法，都是設計成要在（數十個至數百個原子）的大尺度運算中得到最佳的效率。比方說，CASTEP 在大約四百個原子左右的運算規模之下，其計算量與系統大小的比例仍能維持在 N(lnN)。在處理系統大小在數十個至數百個原子之間的雜複問題，CASTEP 所需要的計算資源，恰涵蓋現今標準的工作站至巨量平行處理電腦等不同的硬體平台。因此以計算機硬體條件而言，這樣大小的量子模擬問題都適合用 CASTEP 解決。（其計算資源的代價是否值得則視問題的重要性而定。）

從理論和技術上的層面來講，CASTEP 架構在密度泛函理論之上，把一個極端複雜的多體費米子的問題對映到一個只有單一粒子受到〝交換與相干〞的動態平均場影響。程式本身則以所謂的〝預先調節式的共軛梯度方法〞作爲數值運算的引擎，直接找尋電子結構的基態，它並且利用快速富利葉轉換，在同時在實空間及動量空間進行計算，以避開必須進行矩陣運算的瓶頸，如此構成一個解薛丁格

方程式極有效率的工具。

CASTEP 採用平面波作爲基底來展開波函數，這種基底的特性是單純而穩定，不像使用局域化基底那樣要經過人爲選擇，而發生計算出的物理量會受到基底選擇之影響的不利情況。（基底的收斂性在進行分子動力模擬時特別重要，爲了能有效地重現分子運動真正的軌跡，原子受力的大小與方向在每一個微小時段內，其計算值的收斂都必須迅速而可靠。使用平面波作爲基底，能保證原子受力的計算值具有最佳的收斂性，因此大大地增加分子動力模擬的穩定性。）CASTEP 並且利用贋勢的觀念與方法，把全部電子都必需處理的量子問題，基於量子散射理論作近似，減化爲只需要處理價電子。贋勢的使用，配合上以平面波作爲基底，對進行延伸性、週期性系統的計算有特別好的效能。

（二）CASTEP 的發展過程與歷史背景

CASTEP 是由劍橋大學物理系的凝態理論組所開始發展，最早的版本完成於 1990 年前後。至 1992 年左右略趨完備，當時具備的幾個核心元件，有共軛梯度能量最小化，非局域性的贋勢及其實空間中的演算法，以及分子動力的機制。之後完成的重要改良，尙有簡化金屬計算的熵修正理論與方法，分析晶格對稱性的工具程式介面。

此外，隨著 CASTEP 發展的同時，搭配 CASTEP 計算所需之各種元素的贋勢，也在林志興和本研究案主持人李明憲兩人在英國時期前後主導及努力之下，一方面改進產生贋勢的理論和方法，另一方面針對各式各樣不同的應用環境，來設計出效能和準確性都最佳的贋勢。與 CASTEP 一起發展至今數年，其成果是完成一組產生贋勢的工具程式，以及一個通過嚴格測試的贋勢資料庫，其中匯集了許多元素的贋勢，能提供各種電子結構計算不同的需要。

參與 CASTEP 發展的前後期研究人員頗多，若以幾個較大的事件來看則可大略分爲幾個時期與版本。由於 CASTEP 當時是 Grand Challenge 整合計劃的一部分，使用在愛丁堡的 Intel i860 平行電腦，劍橋也與愛丁堡合作，爲 i860 平行電腦改寫一個 CASTEP 的初期平行化版本，叫做 CETEP ，當時的成員則成爲現在的 UKCP 委員會，各自繼續使用並發展程式。CASTEP 也是當時英國 CCP 計劃中的 CCP9 ，並曾在 1993 年舉辦過一次夏季學校，對有興趣參與的學者們發表，幾乎英國重要的電子結構計算的研究群，來自劍橋、牛津、愛丁堡、基爾、巴斯、倫敦大學，以及數個歐洲國家的研究機構，都派人參加，學員的研究領域，涵蓋固態物理、表面化學、地球科學、材料冶金。除了這些因計劃產生的使用者之外，CASTEP 開發的過程中也有零星的新成員加入取得程式，以進行

其各自有興趣之計劃。

在 CCP9 完成之後，由於受到相關基礎科學及應用科技人士之熱列回響，面對潛力豐富的工業應用，以及爲了擴大影響力，替理論發展本身尋求更好的支援。劍橋 CASTEP 研究群，授權給業界有名的科學計算軟體公司 Molecular Simulation Inc.（MSI）來包裝及發行 CASTEP 的商業版，對象主要爲工業界及其他對只希望使用 CASTEP，卻無興趣研發的使用者。MSI 在 CASTEP 的主要工作，是將 CASTEP 已經完成了的各種功能模組整合起來，並與該公司的主力 3D 視覺化圖形介面 Cerius2 結合，使所有的計算準備以及結果的呈現與分析，都能夠在一個專爲非行家設計的圖形介面下進行。另一方面，MSI 也致力於在工業界發掘可能 CASTEP 課題，回饋給發展的成員，以作爲改良與突破的目標。至於最佳化膺勢資料庫的部分，MSI 亦獲得授權使用，資料庫中膺勢的更新測試與膺勢方法的研發改良，則繼續由本研究案主持人李明憲與合作者林志興教授負責。

研究步驟

（一）硬體準備及軟體參數設定之基礎測試

凡是高品質的電腦模擬研究必定都要有周延的準備工作。計畫一開始我們即對將使用的軟體、硬體，以及理論近似的選項都作了測試。事實上，這一階段的重點也包含對碩士生兼任研究助理在操作各種程式上的訓練。

（二）建立高分子鍊及相關分子團之三度空間結構模型

我們利用 Cerius2 介面裏的 Builder 來建立分子團單元與完整的週期性高分子長鍊，同時確定總共要模擬的分子團種類及數目。凡是有需要加氫或其他原子作終端的動作，都在此一階段完成。

（三）高分子及單元分子團以力場方法進行結構最佳化

在建構出合理的分子單元之後，我們要利用力場方法先進行初步的結構最佳化。雖然其結構尚未完全正確，但將可大幅減少在量子計算時所消耗的時間。

（四）無吸附金屬表面量子計算及原子軌域投影定出最佳吸附位置

如果分子在金屬表面上的吸附位置不知道，那麼以量子科學方法針對可能的不同吸附位置去一一計算是極爲費時的。爲了能夠預測出能量最低、鍵結最強的吸附位置，我們要針對無吸附表面先進行一次量子計算，利用原子軌道投影方法得知費米面上下的能態在金屬表面是來自那些電子雲區域的貢獻，這就表示該處將是化學鍵形成最有利的位置。有了此一訊息，我們可以輕易地把前一步驟已架構好之分子結構直接植入到金屬表面上，以此作爲進一步量子化學吸附之初始結構。

（五）有分子吸附的全套量子力學金屬表面計算與鍵結分析

本研究最終的目標是要探討是要在精確重現金屬表面性質的情況下，了解不同化合物分子單元在鍵結上的不同效應與對吸附力的差異關係。因此我們必須進行一系列化學吸附的量子計算並從鍵能及電子雲分佈的角度來對不同的官能基分子團作比較分析。

研究資源規劃

計算進行所需要的計算機資源，是向國家高速電腦中心申請，此外本研究小組現有的硬體資源，六顆數值運算處理器的平行工作站也被作爲執行計畫的主要平台，因此硬體支援尚屬足夠。在軟體方面，本研究小組爲程式發展成員之一，因此更沒有問題。

在人員人力的規劃上，計畫主持人本身負責模型的建構以及進度的掌控，指導參與研究之助理人員熟悉 CASTEP 程式的理論及操作，並他們的協助下主導文獻搜集、研讀以及計算結果的分析工作的。而包含在計畫之中的人員訓練講習，也將申請人親自主持。主要實作工作項目，在於在對金屬進行表面能帶結構計算的同時，進行一系列不同之高分子鍊上之分子團對它的吸附計算，從結果我們將可以得到各種分子團在整體黏著力所扮的角色。

本計畫之執行期限規劃爲一年，爲了要在一年之內完成，主要助理人員在量子力學及固態物理的基本知識要足夠，才能節省執行的時間，故原本依需要而規劃一名碩士級專任助理。旁支的部分，例如不同金屬時的吸附能力，由於可以依循鐵金屬表面的研究模式，故需要的人力時間較少，但有鋁系統及鋅系統兩類，故以一名碩士班學生兼任研究助理來協助，負責跑程式、分析數值及比較。然而實際經費的核定上，未能獲得專任助理之補助，但基於珍習計畫獲得通過的機會，仍然決定全力以赴，盡力而爲。

助理研究人員本身經驗的不足及時間不足，在計畫的執行中的確造成不利與不便。這是因爲兼任助理由現正在學之學生擔任，其個人在校內有助教課及一般性的學習，因此投入計畫案研究的時間會受到壓縮，會而導致在進度控制時壓力較大。尤其是恰逢本研究群去年舊生畢業，所有成員皆爲新生，指導訓練其入門及理論與計算實作並重，皆需要一段時間。計畫之初期如果未能上手而循序將計算工作送入電腦之中，則也會造成整體可用計算時間之減少。固然計畫主持人應負時間掌控之責任，但真實的情況的確造成在進度方面未能如最初預期之快速，而且是人力的因素爲主。

研究過程中波函數及電荷密度等大量資料的貯存，故工作站本身即需要擴充硬碟，已由計畫中之補助經費購置。凡是已經完成的單項計算，更需要從電腦系統中移走，故也採購了需要的可抹寫光碟片及碟帶等貯存媒介。但是原本基於專作爲圖形處理的工作站的記憶體不足，導致作圖時總是耗費保貴時間，故希望能酌量追加 128Mb 之記憶體，以利作圖之想法，則因計算時間之限制而造成放棄計

算最大之完整高分子鍊結構，因而尚未用上。我們已經在明年度的計畫中，重新規劃最大完整高分子鍊結構之計算，因爲今年參與計畫的成員已經經過了整整一年的理論分析方法學習以及實際操作經驗，我們對於在明年補完此一計算具有高度的信心。

結果分析

吸附位置 beidge & top site 比較

本研究案在初期測試的階段，爲了建立精準之吸附鍵能，曾經比較測試過同樣分子在不同的吸附位置上的能量，所獲得的結論是：對於所選定的鋁金屬 (100) 面而言，在原子正上方有最強的鍵結。對於本研究案中爲了簡化計算而建構的鐵鋁系統而言，最佳吸附點亦位於鐵原子之上。這使得我們在模型的建構上得以沒有予盾。

分子吸附於鋁表面

由於可能的吸附有兩種，一種是氫原子和官能基一樣留在表面上，另一種狀況是氫原子先行解離於官能基之外，再以離子化之官能基吸附於金屬之上。以一般常理來推想，是前者較有可能。而本案則針對兩種況狀都進行計算，一則是爲了獲得定量上的比較，二則是是不含共吸附氫在同一模擬計算中量子態的分析較容易進行。

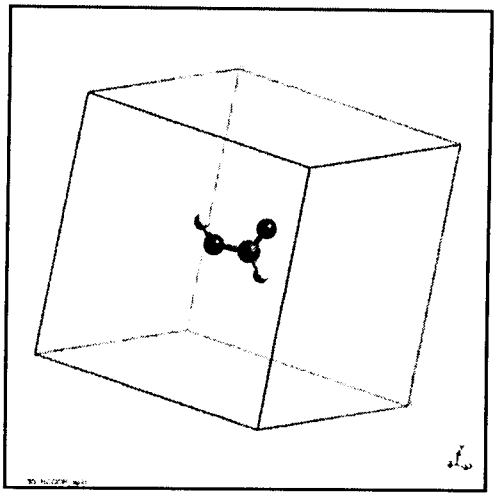
以下四頁中

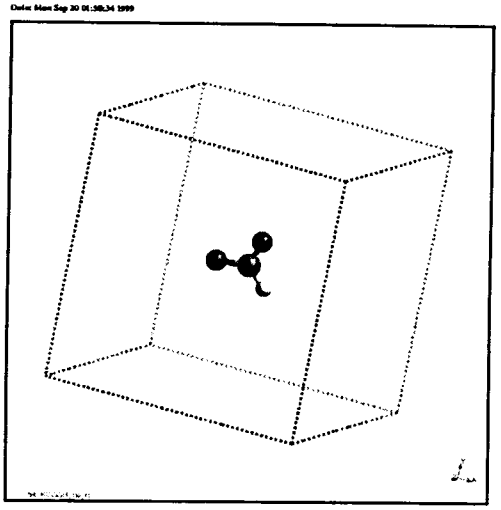
第一頁右上圖爲甲酸分子的模型，左上圖爲甲酸分子游離一個氫的模型。右下圖爲磷酸分子的模型，左下圖爲磷酸分子游離一個氫的模型。

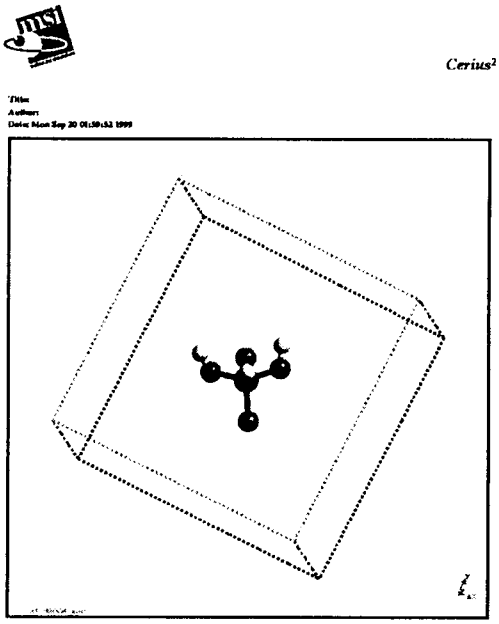
第二頁右上圖爲甲烷分子的模型，左上圖爲甲烷分子游離一個氫的模型。右下圖爲醋酸分子的模型，左下圖爲醋酸分子游離一個氫的模型。

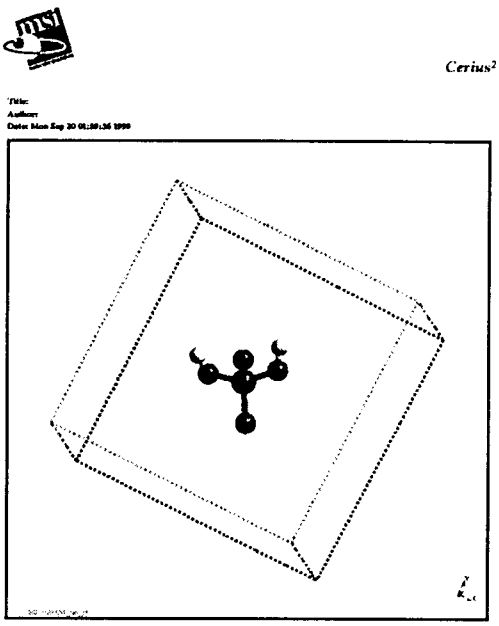
第三頁是不含磷酸根的高分子鍊模型。

第四頁是含磷酸根環氧樹脂的高分子模型。


Cerius²

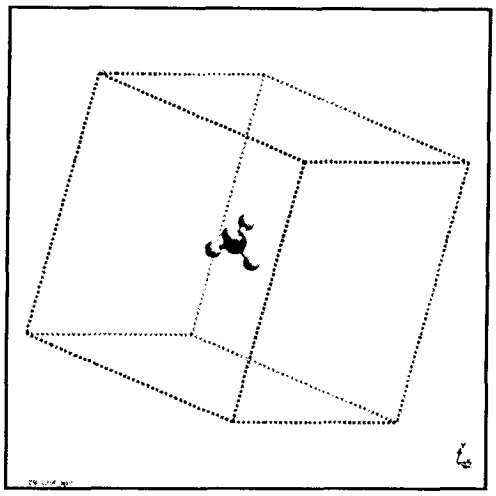

Cerius²


Cerius²


Cerius²

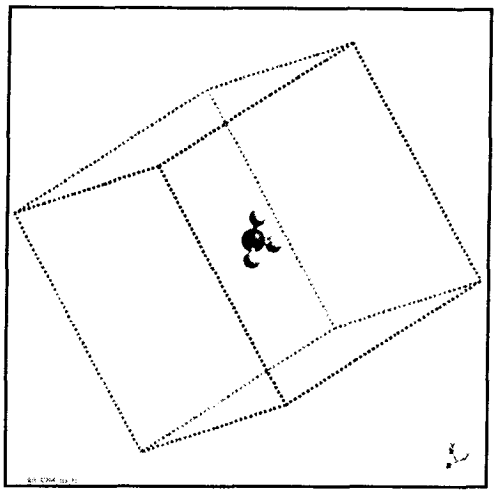
Cerius²

Title:
Author:
Date: Mon Sep 20 08:00:08 1999



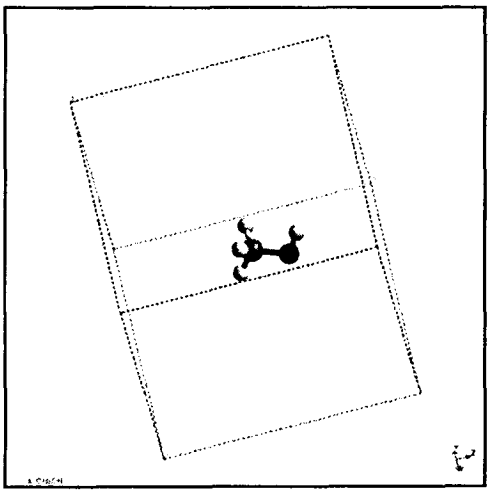
Cerius²

Title:
Author:
Date: Mon Sep 20 08:00:28 1999



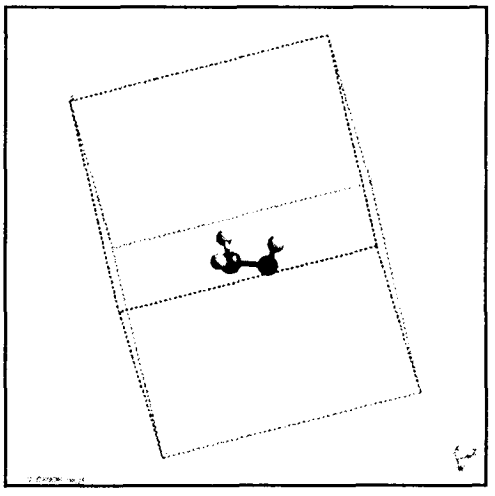
Cerius²

Title:
Author:
Date: Fri Sep 24 08:49:53 1999



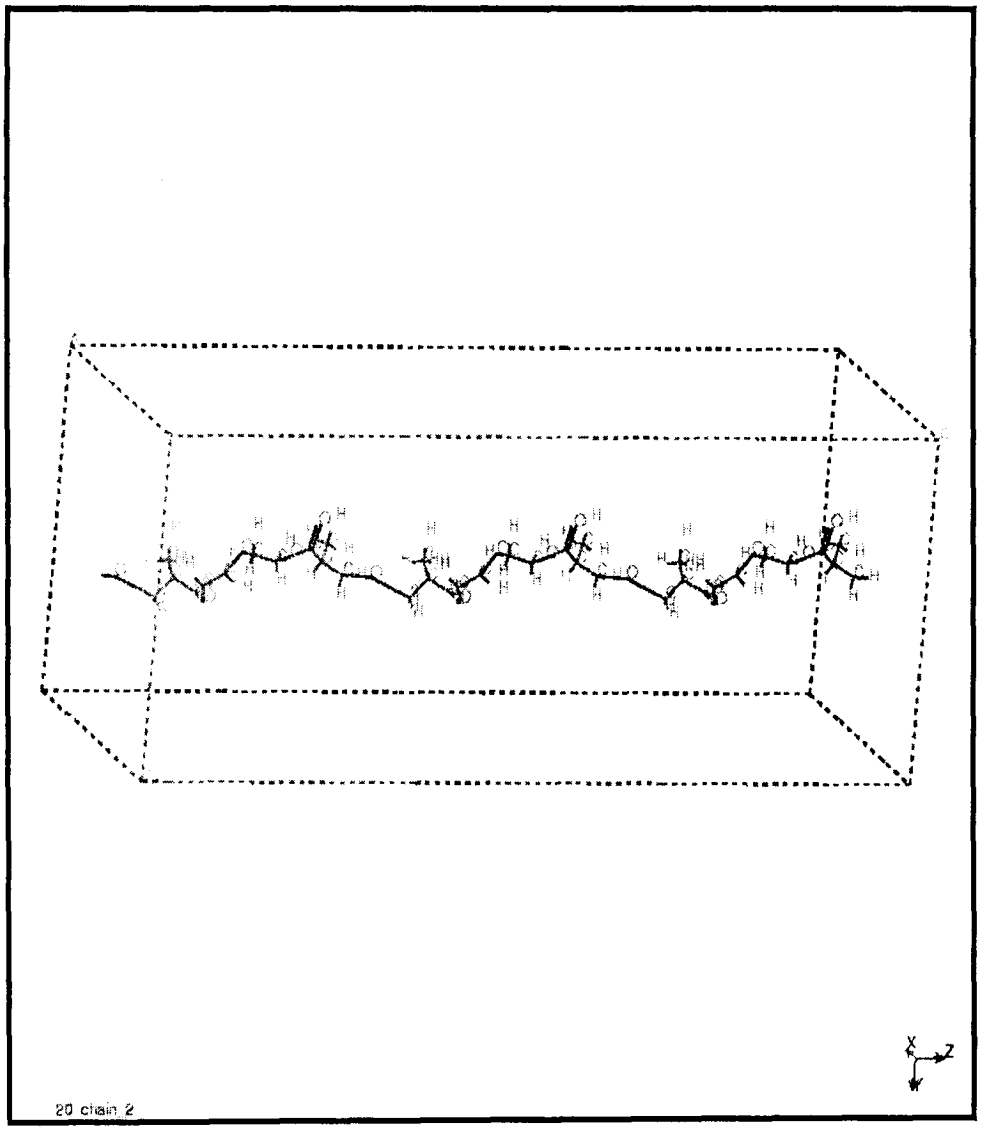
Cerius²

Title:
Author:
Date: Fri Sep 24 08:50:07 1999



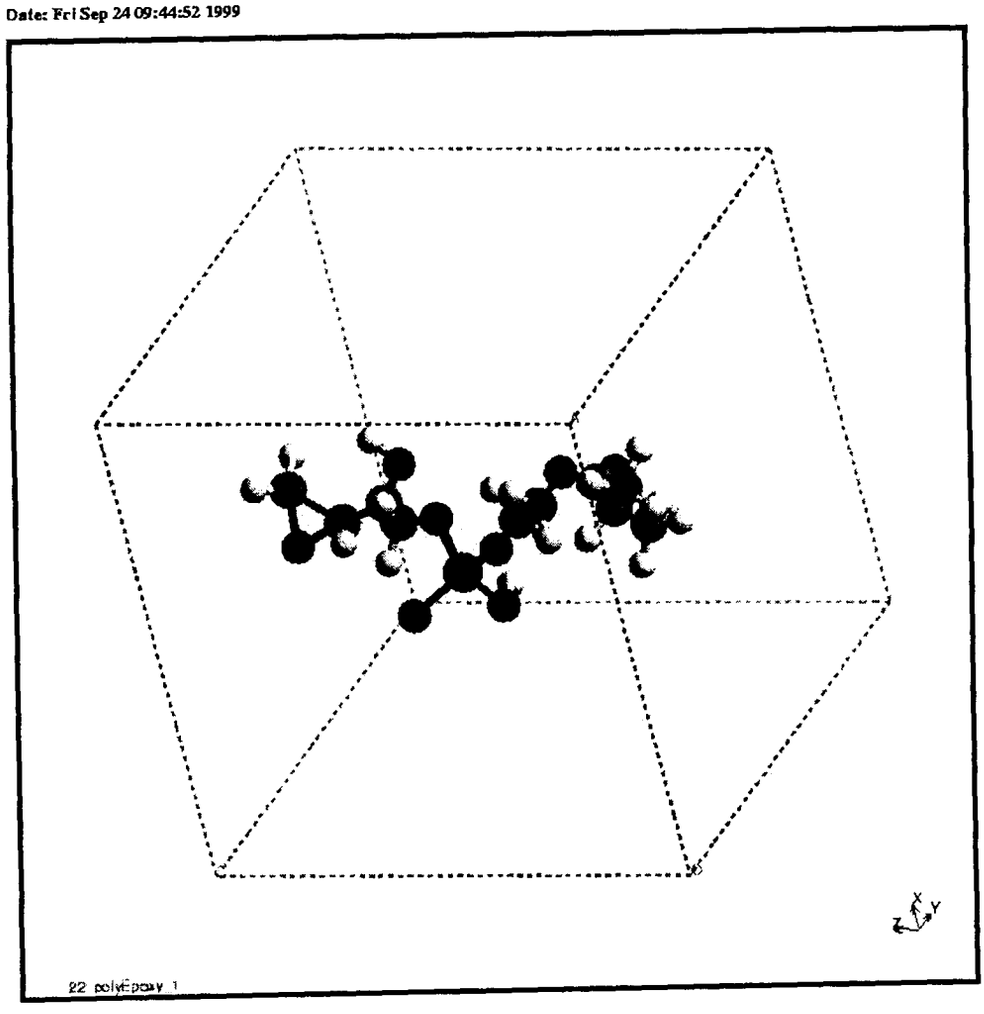
Cerius^2

Title:
Author:
Date: Fri Sep 24 09:49:09 1999



Cerius^2

Title:
Author:
Date: Fri Sep 24 09:44:52 1999



以下三頁中

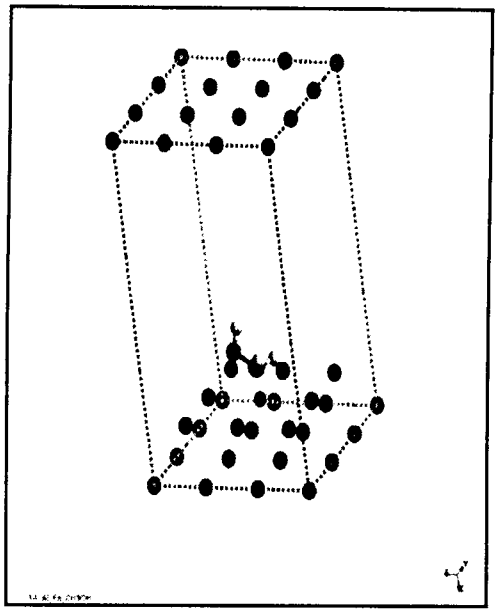
第一頁右上爲脫氫分子 CH3O 吸附在鋁表面。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的碳與表面的鋁之間的鍵結。也可從等密面圖中看到。

第二頁爲表面有鍵結的鋁 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中碳的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

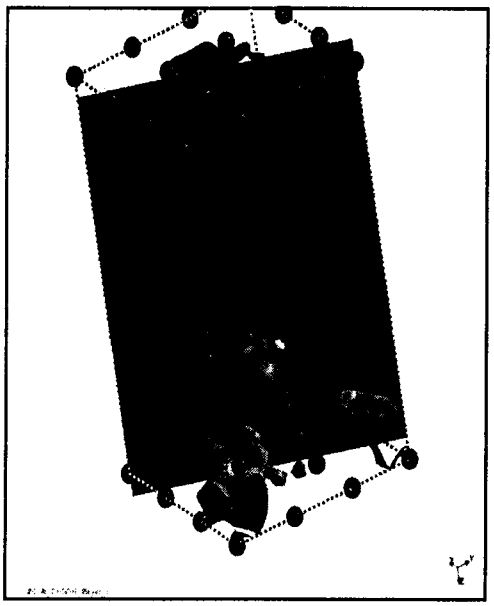
Cerius^2

Title:
Author:
Date: Mon Sep 20 08:08:07 1999



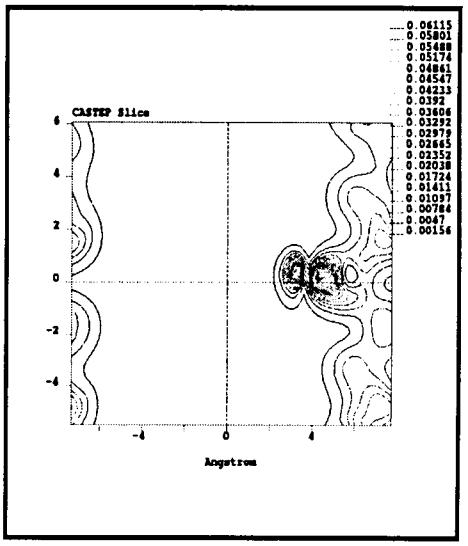
Cerius^2

Title: Al_CH3OH_2layer_010
Author:
Date: Fri Sep 24 02:10:48 1999

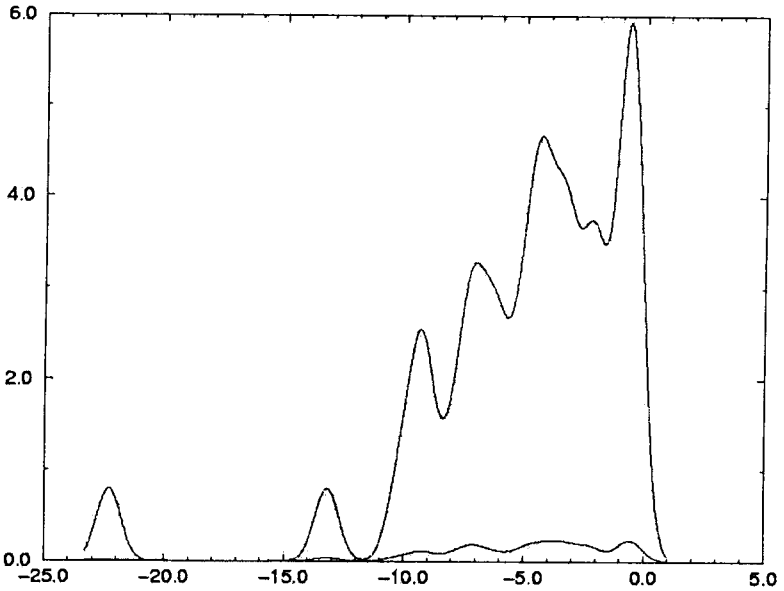


Cerius^2

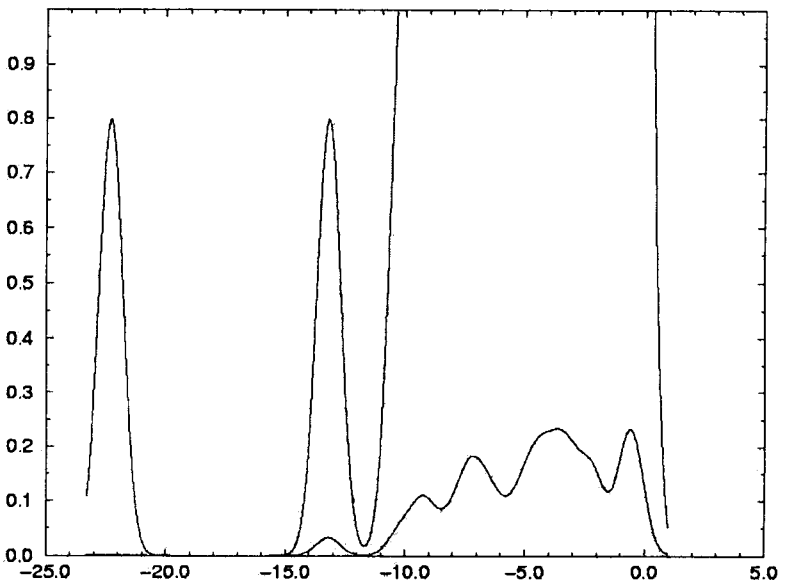
Title: Al_CH3OH_2layer_010
Author:
Date: Fri Sep 24 02:12:14 1999



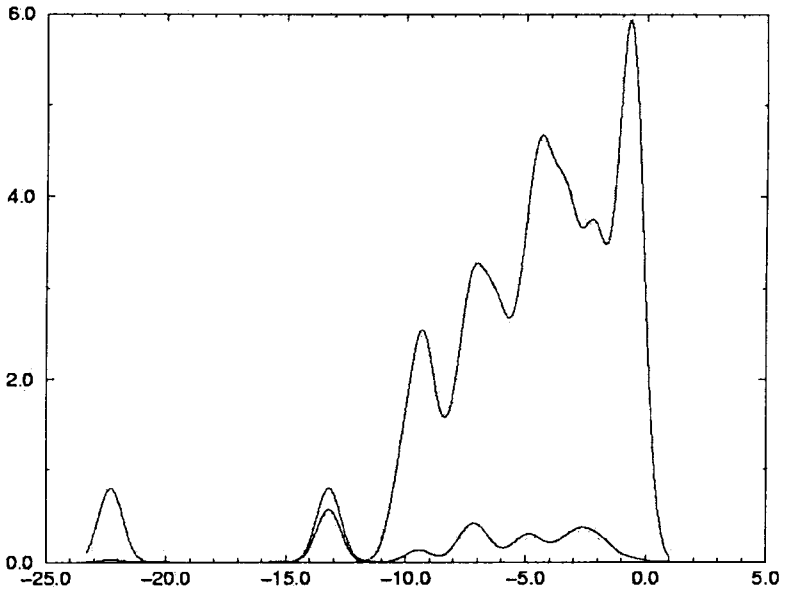
CH3OH Al The Al



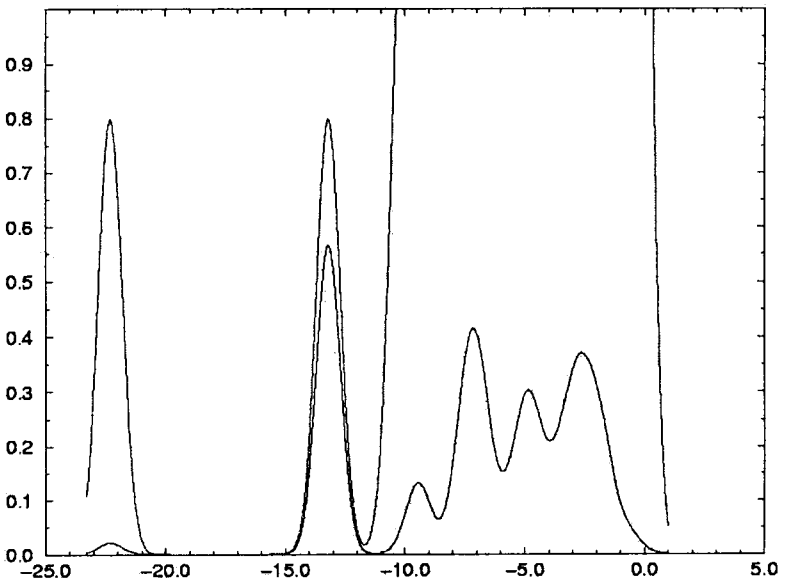
CH3OH Al The Al



CH3OH Al C



CH3OH Al The Al



以下三頁中

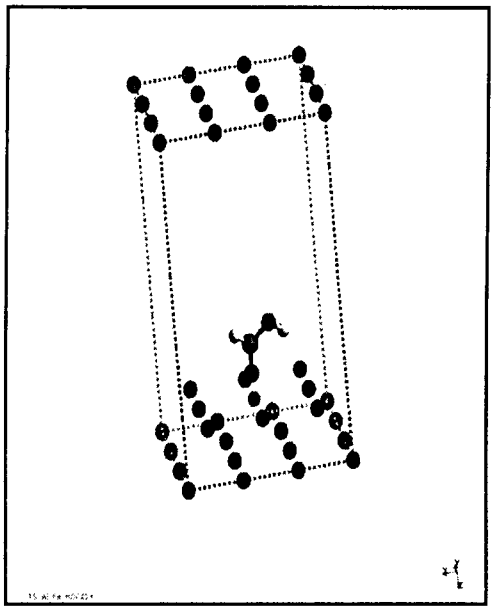
第一頁右上爲脫氫分子 HCOO 吸附在鋁表面。左下是 total density 等密面圖，可很明顯地看到電子軌域的形狀，右下是此剖面圖。由這等密面圖可從中看到電子雲分佈的形狀，跟表面的形狀非常吻和，又由密度等高線圖，可看出鍵結極其微弱。

第二頁爲表面有鍵結的鋁 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中氧的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

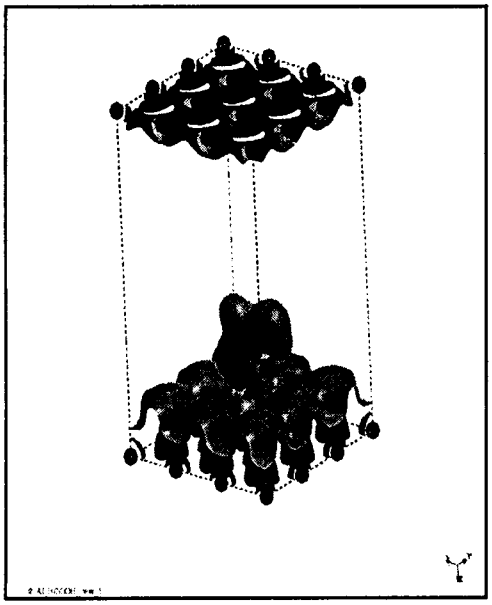
Cerius²

Title:
Author:
Date: Mon Sep 20 02:06:36 1999



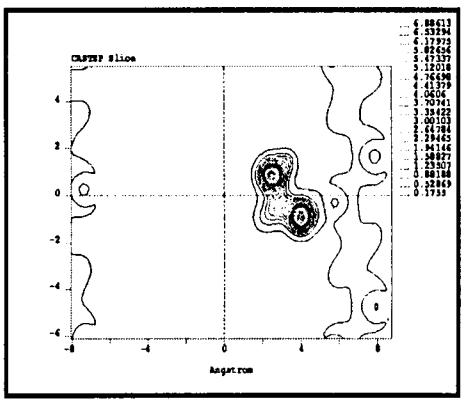
Cerius²

Title: Al_MCOOH_2layer_Total Density
Author:
Date: Fri Sep 24 11:19:46 1999

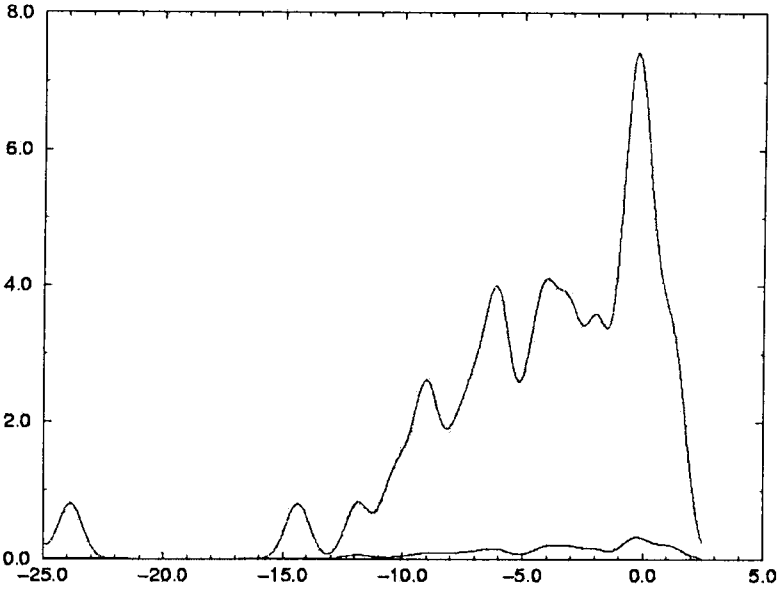


Cerius²

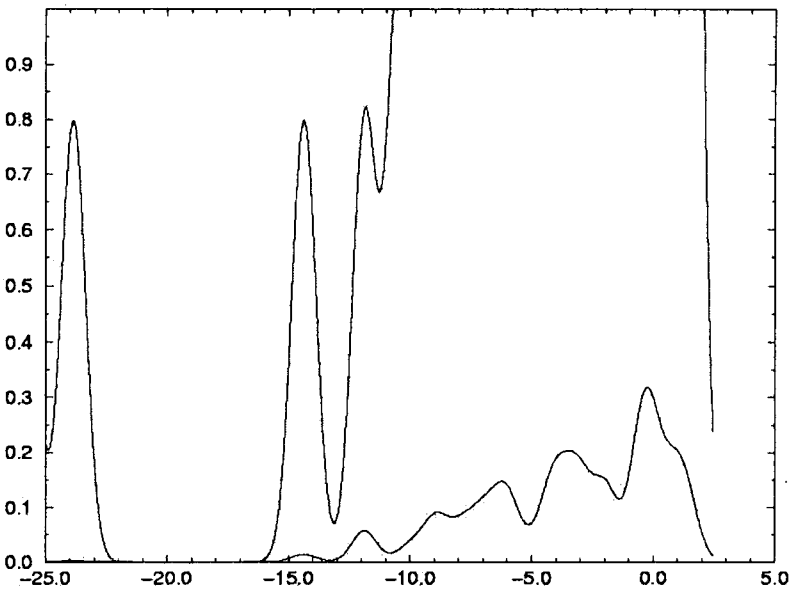
Title: Al_MCOOH_2layer_Total Density
Author:
Date: Fri Sep 24 11:21:38 1999



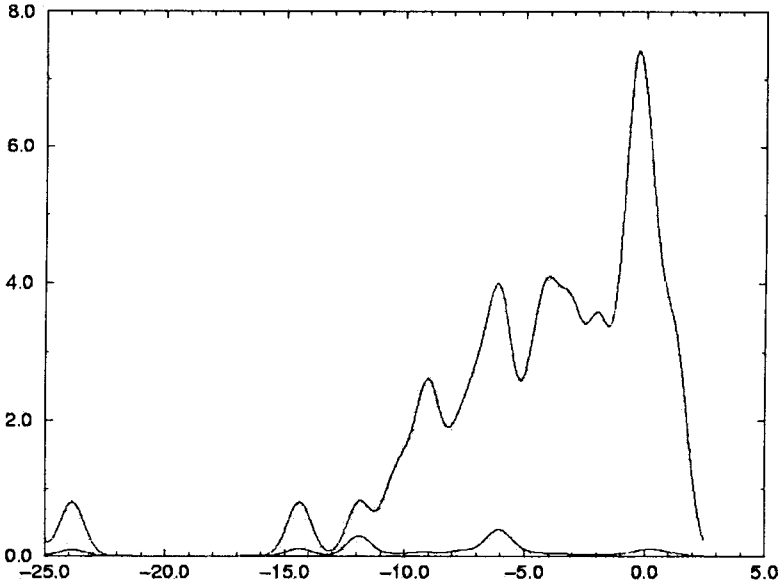
HCOOH Al The Al



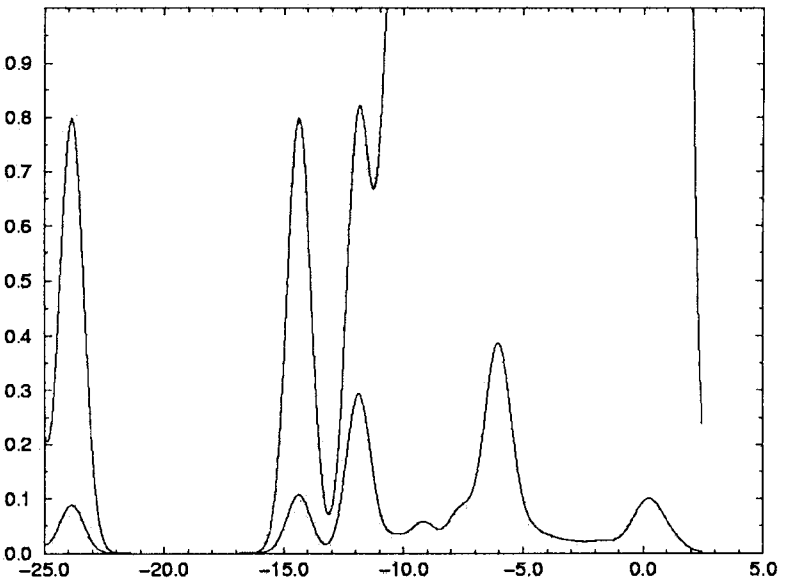
HCOOH Al The Al



HCOOH Al The O



HCOOH Al The O



以下三頁中

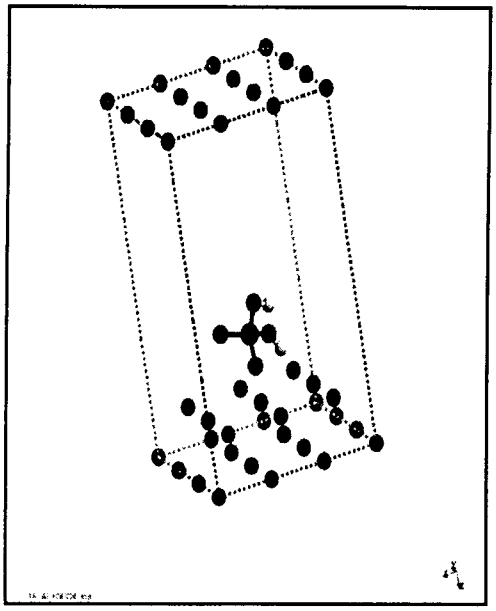
第一頁右上爲脫氫分子 H2PO4 吸附在鋁表面。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的氧與表面的鋁之間的鍵結。也可從等密面圖中看到。

第二頁爲表面有鍵結的鋁 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中氧的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

Cerius²

Title:
Author:
Date: Mon Sep 20 08:04:37 1999



Cerius²

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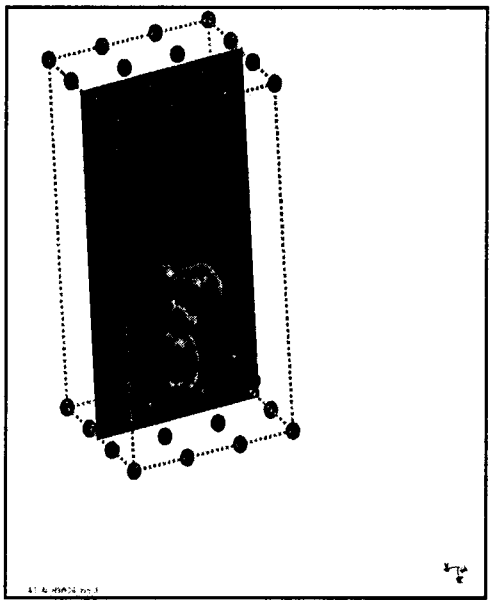
Author:
Date: Fri Sep 24 08:14:54 1999



Cerius²

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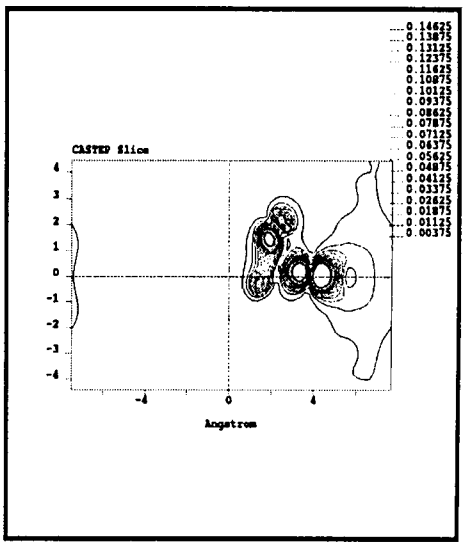
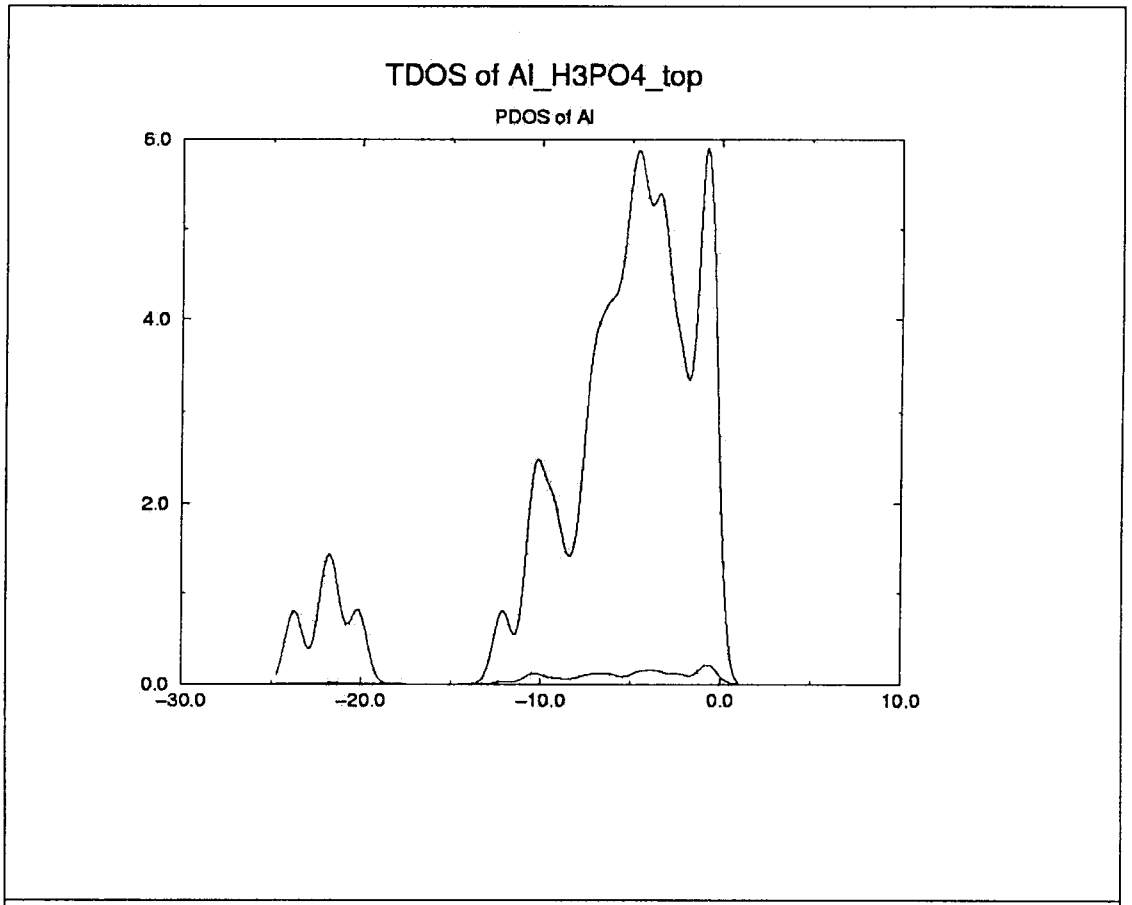
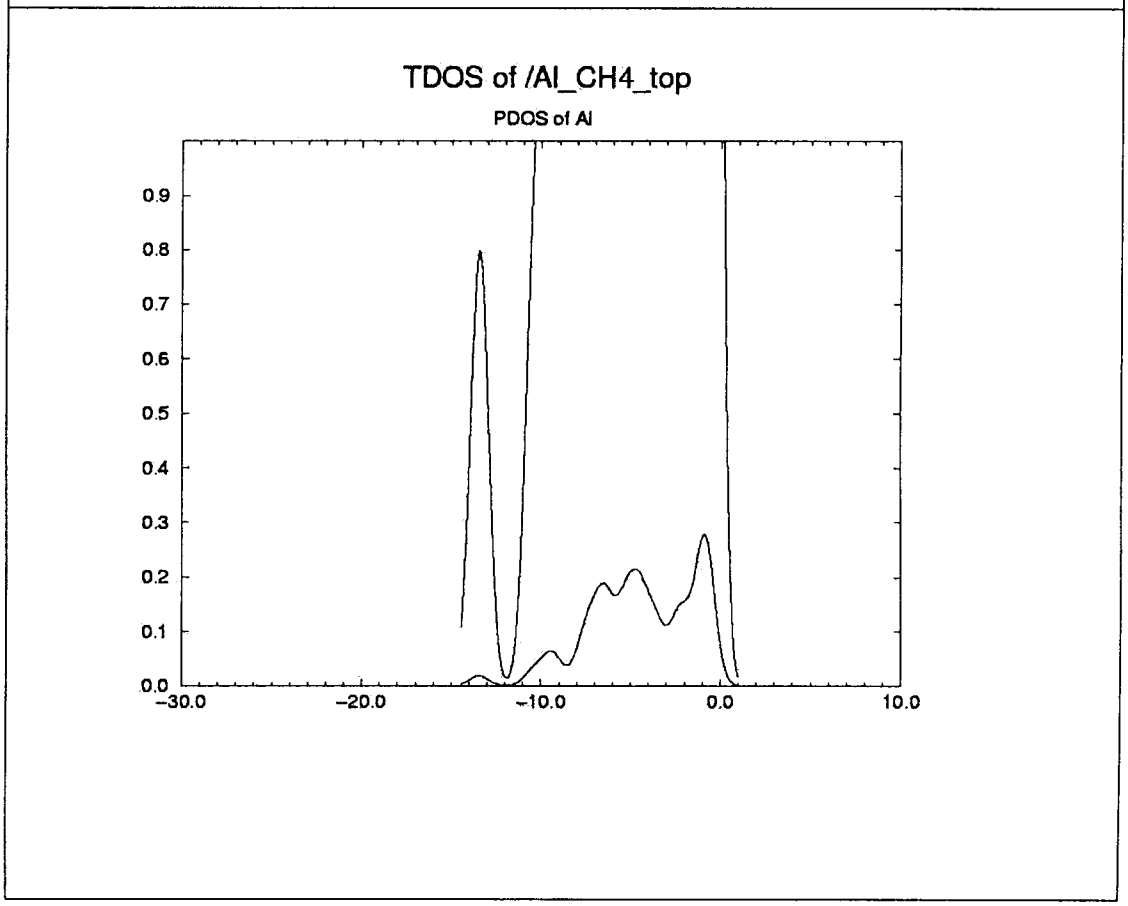
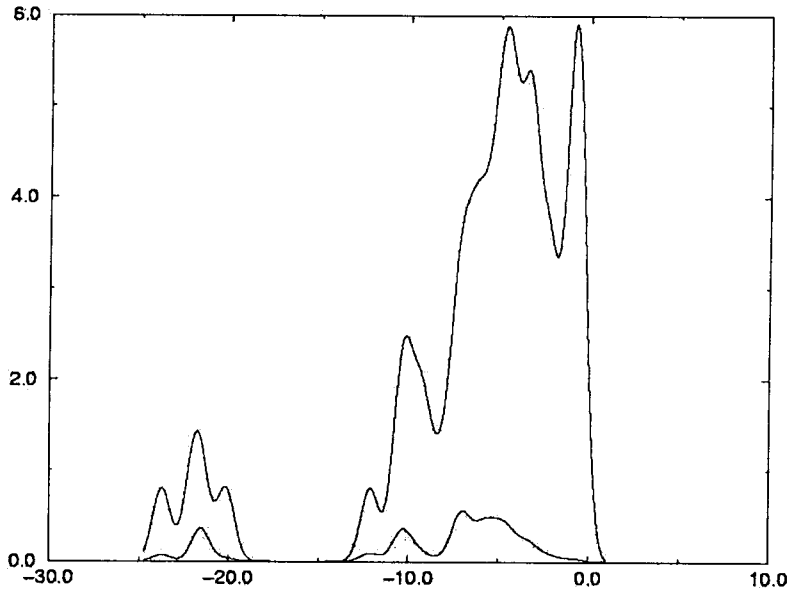
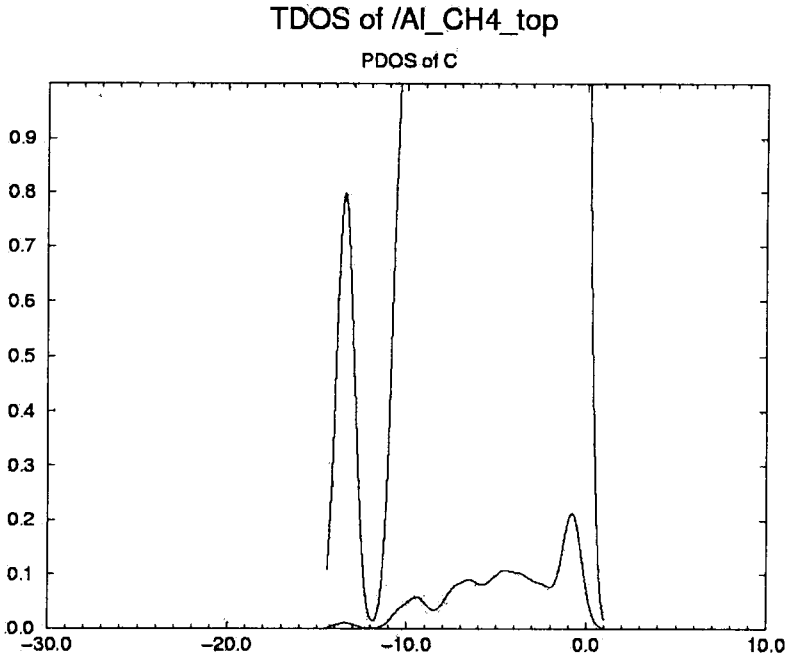
Author:
Date: Fri Sep 24 08:15:38 1999




TDOS of Al_H3PO4_top
PDOS of Al
6.0
4.0
2.0
0.0
-30.0
-20.0
-10.0
0.0
10.0


TDOS of /Al_CH4_top
PDOS of Al
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-30.0
-20.0
-10.0
0.0
10.0


6.0
4.0
2.0
0.0
-30.0
-20.0
-10.0
0.0
10.0


TDOS of /Al_CH4_top
PDOS of C
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-30.0
-20.0
-10.0
0.0
10.0

以下三頁中

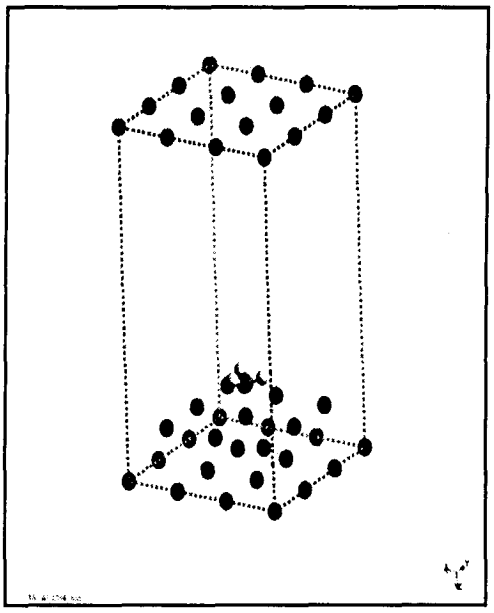
第一頁右上爲脫氫分子 CH3 吸附在鋁表面。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的氧與表面的鋁之間的鍵結。也可從等密面圖中看到。

第二頁爲表面有鍵結的鋁 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中碳的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

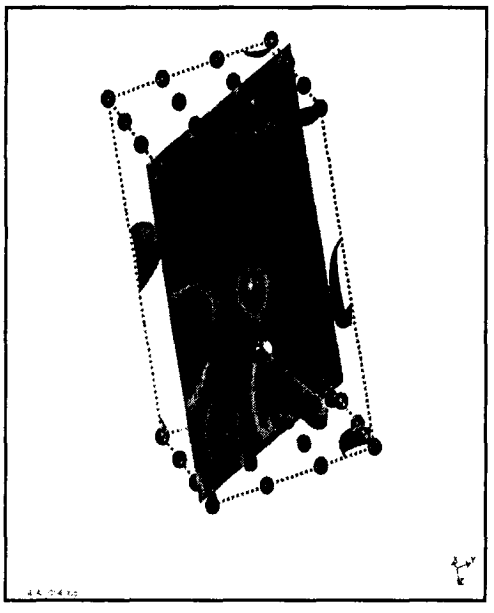
Cerius²

Title:
Author:
Date: Mon Sep 20 02:08:56 1999



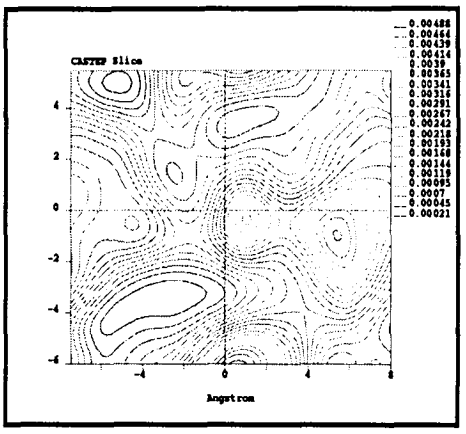
Cerius²

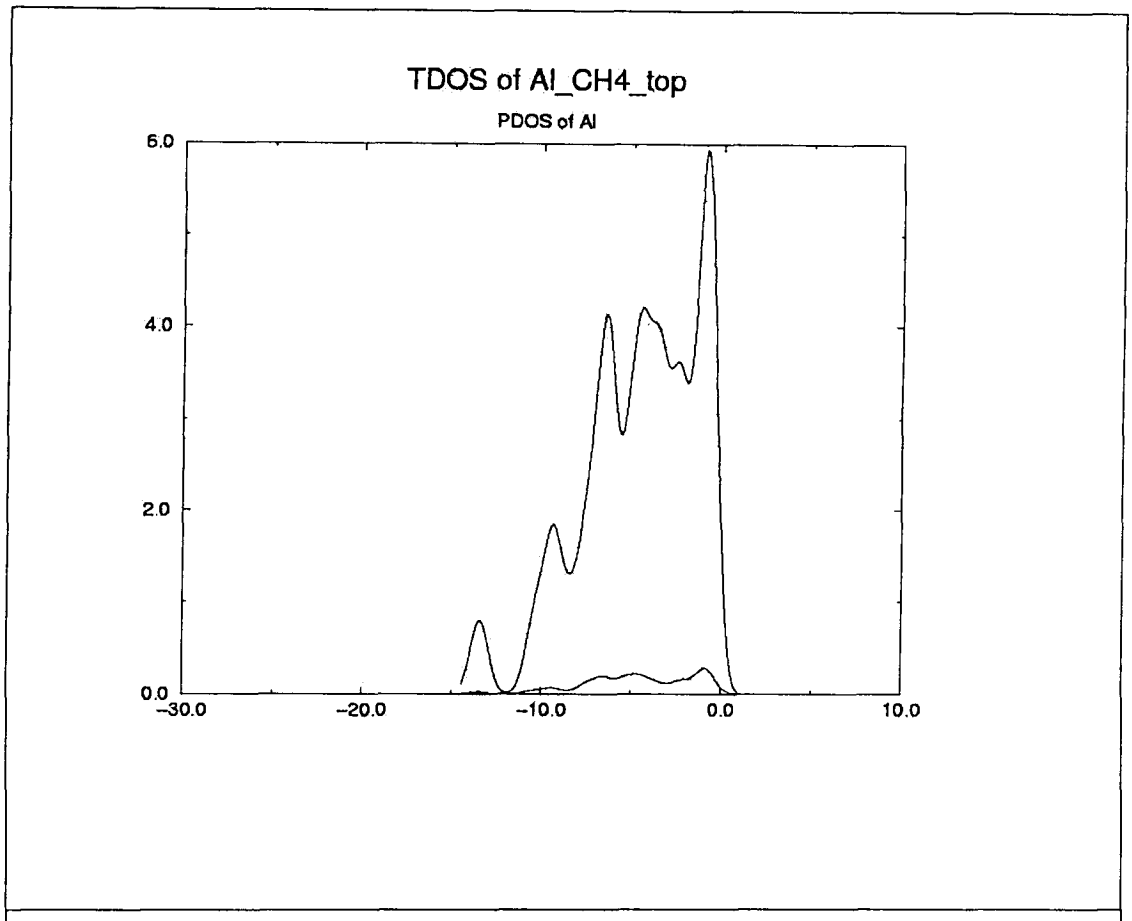
Title:
Author:
Date: Thu Sep 23 10:28:27 1999

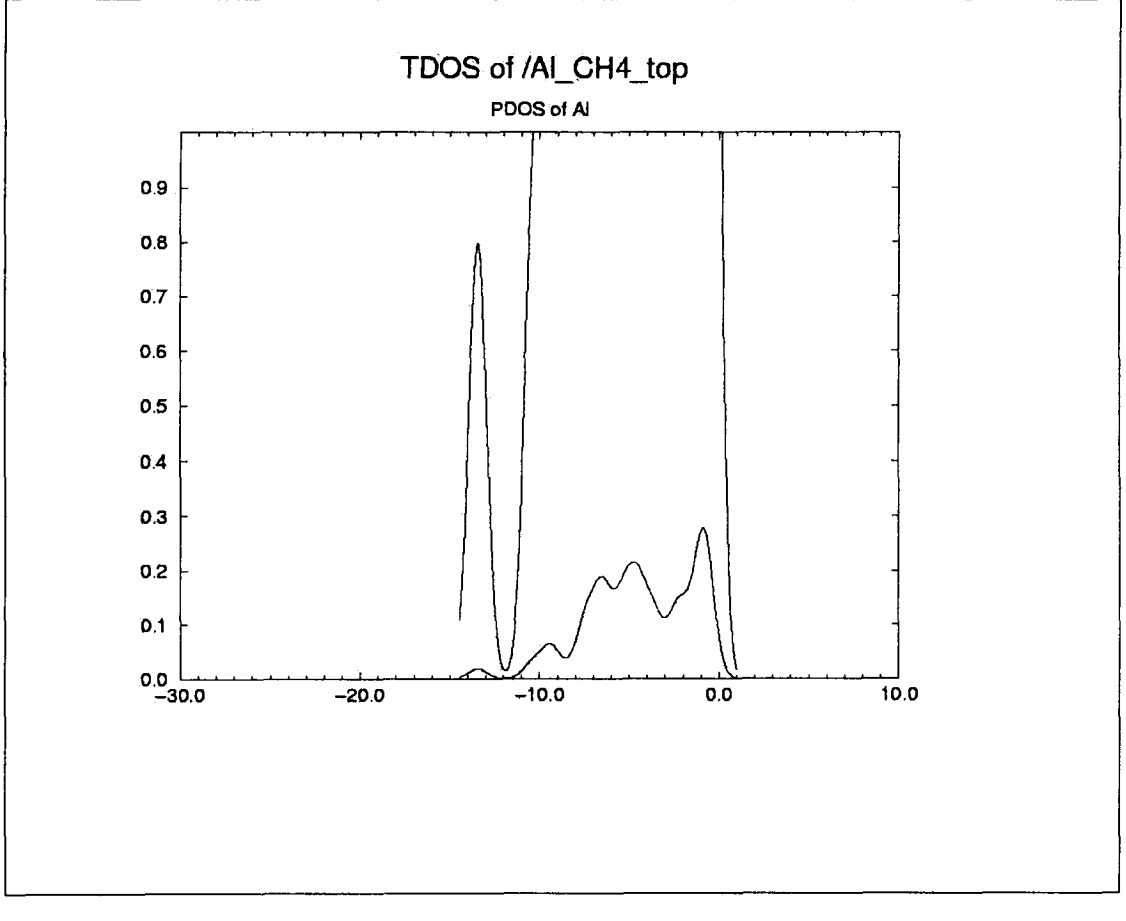


Cerius²

Title: Al_CH4_top_graph
Author:
Date: Mon Sep 20 15:34:45 1999




TDOS of Al_CH4_top
PDOS of Al
6.0
4.0
2.0
0.0
-30.0
-20.0
-10.0
0.0
10.0


TDOS of /Al_CH4_top
PDOS of Al
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-30.0
-20.0
-10.0
0.0
10.0

分子吸附於鐵取代鋁表面

所謂的鐵取代鋁，意指我們在建構模型時仍以鋁原子排列成表面結構，而僅在與分子片段形成鍵能位置上的鋁原子將之更換成爲鐵原子。如一安排的目的在於，在不增加加太多計算時間的狀況之下，仍可讓金屬表面開始表現出鐵的特性。當然這已經是一大近似，未來待研究之深入程度需要更進一步，則我們可以在現有的方法步驟規劃下馬上引入全鐵原子的計算。

以下三頁中

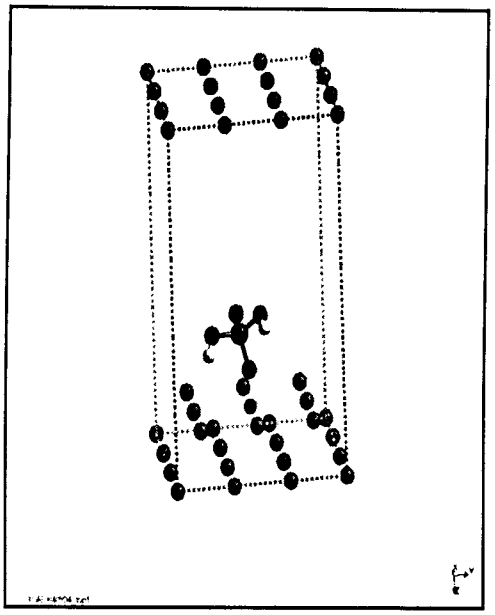
第一頁右上爲脫氫分子 H2PO4 吸附在鋁表面，但注意的是鋁表面其中一個鋁改換爲鐵。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的氧與表面的鐵之間的鍵結，其中含有 π 鍵。也可從等密面圖中看到。

第二頁爲表面鐵的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中氧的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

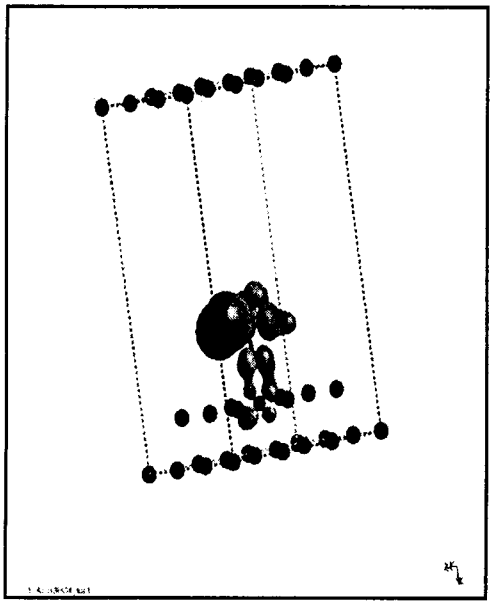
Cerius²

Title:
Author:
Date: Mon Sep 20 08:22:40 1999



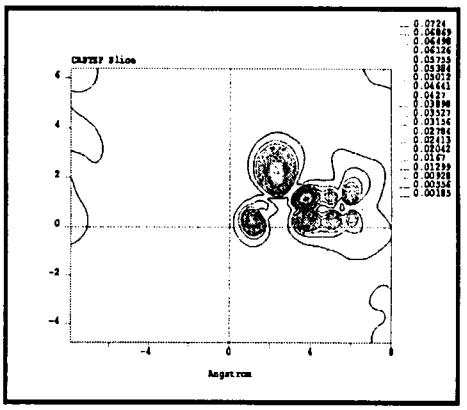
Cerius²

Title:
Author:
Date: Wed Sep 22 21:03:28 1999

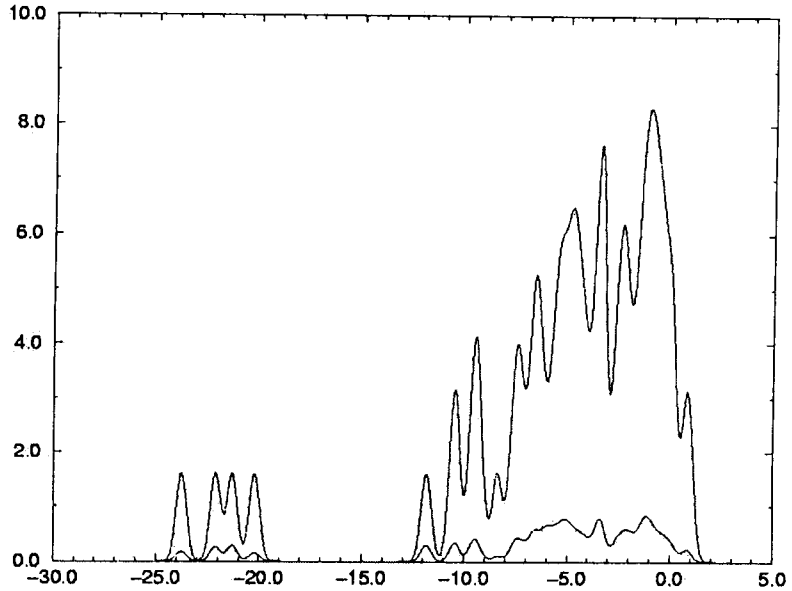


Cerius²

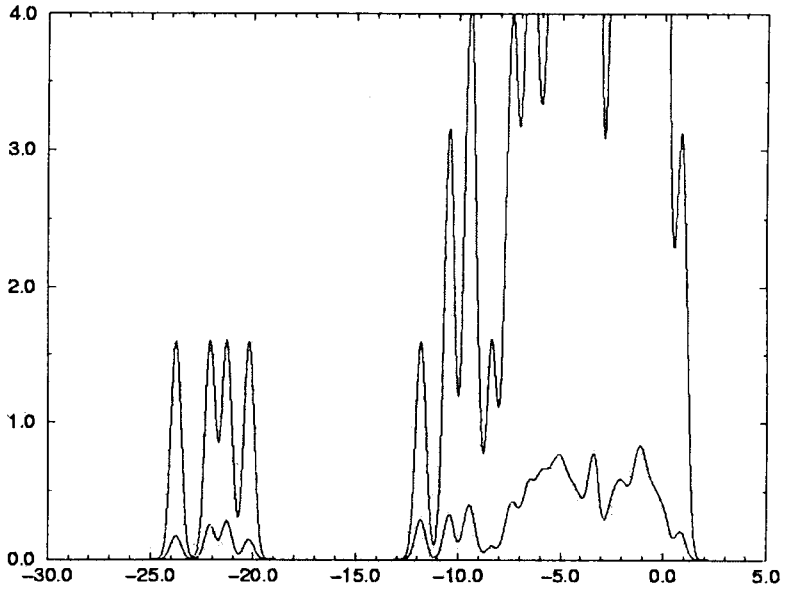
Title:
Author:
Date: Wed Sep 22 16:46:07 1999



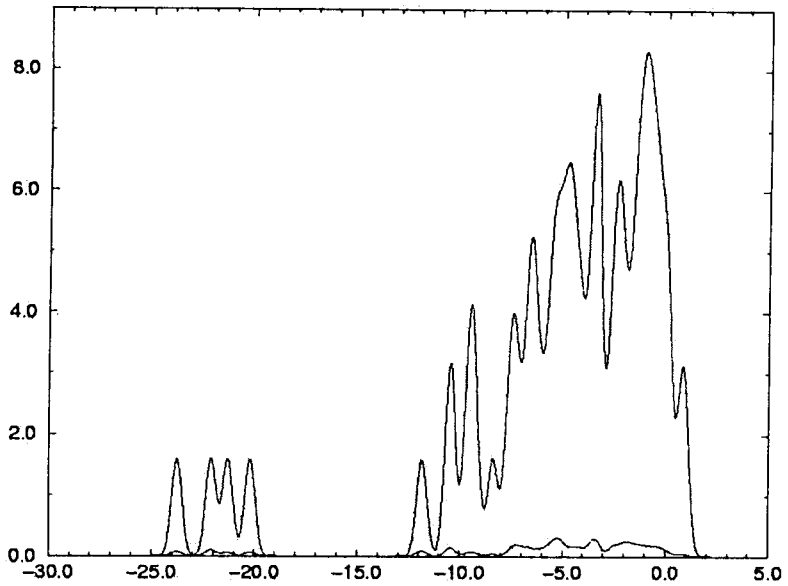
H3PO4 Fe_all



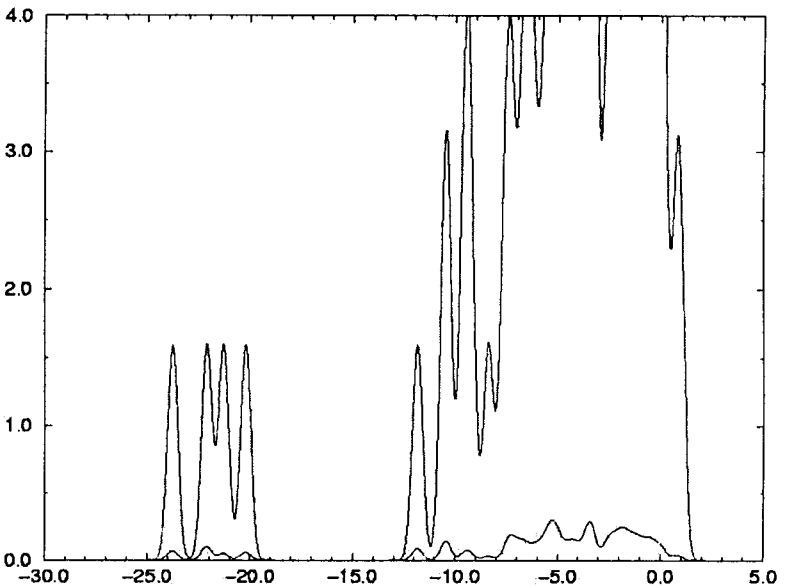
H3PO4 Fe_all



H3PO4 O_all



H3PO4 The O



以下三頁中

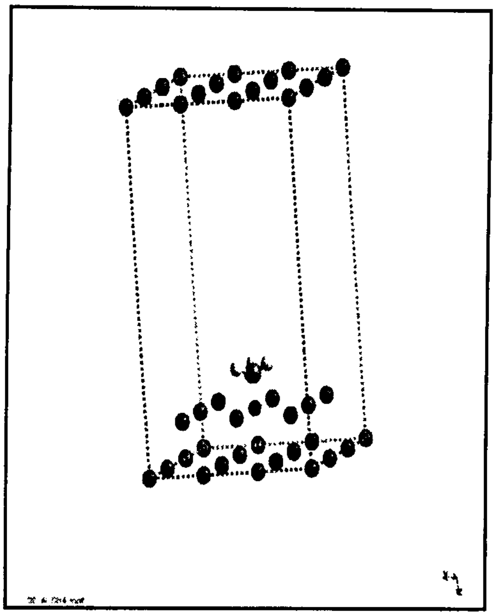
第一頁右上爲脫氫分子 CH3 吸附在鋁表面，但注意的是鋁表面其中一個鋁改換爲鐵。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的碳與表面的鐵之間的鍵結。也可從等密面圖中看到。

第二頁爲表面鐵的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中碳的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

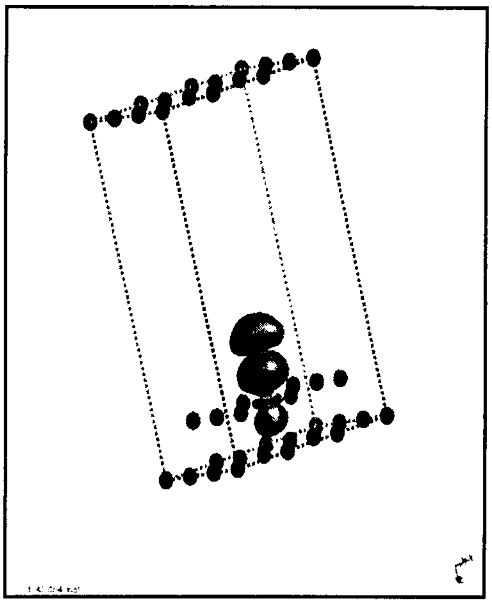
Cerius^2

Title: Al_CH3OH_2layer_010/-6.826–6.824ev
Author:
Date: Fri Sep 24 06:21:54 1999



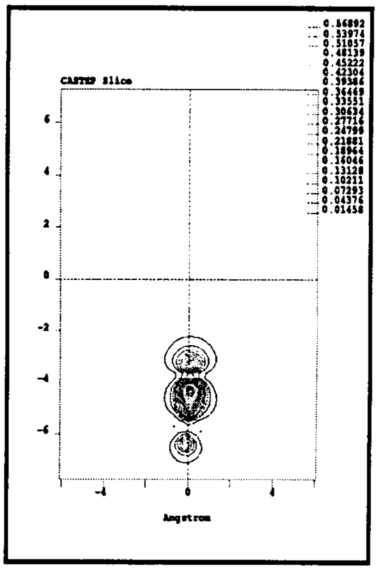
Cerius^2

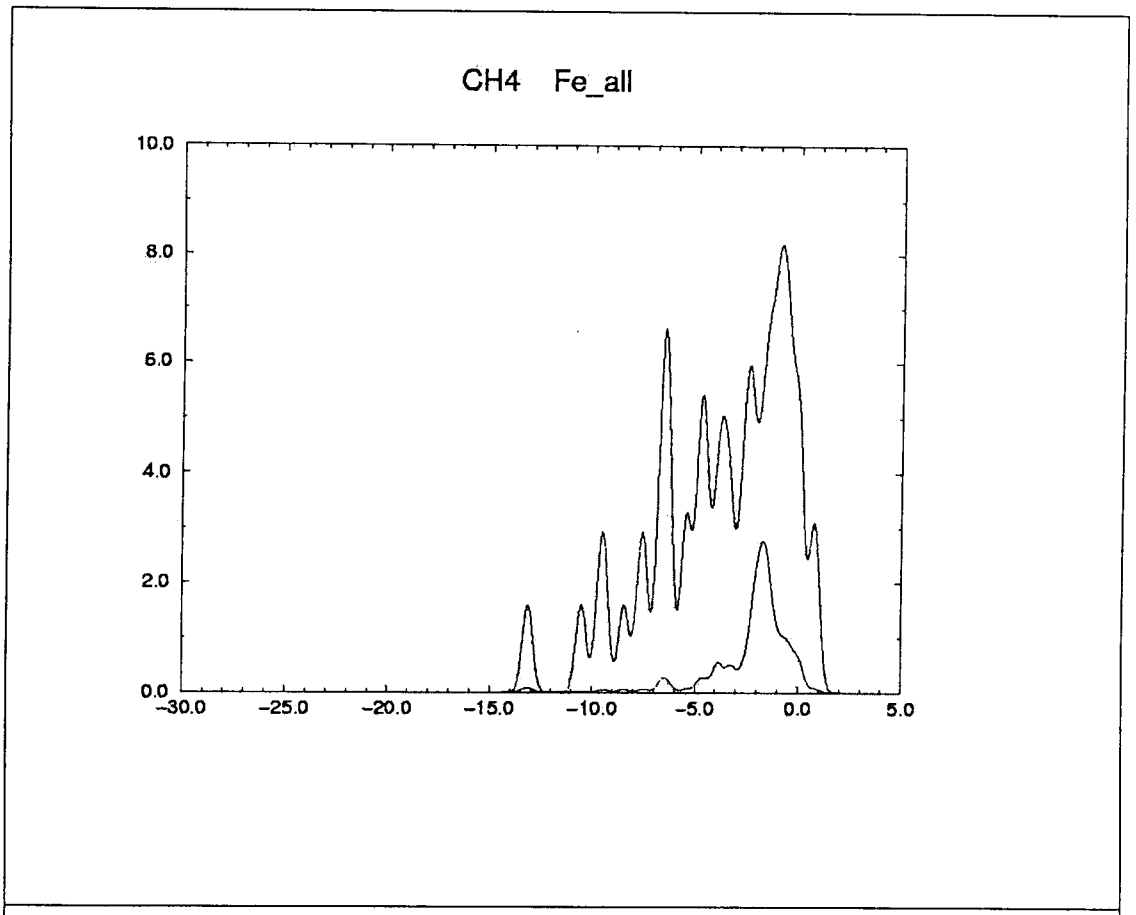
Title:
Author:
Date: Wed Sep 22 20:50:24 1999

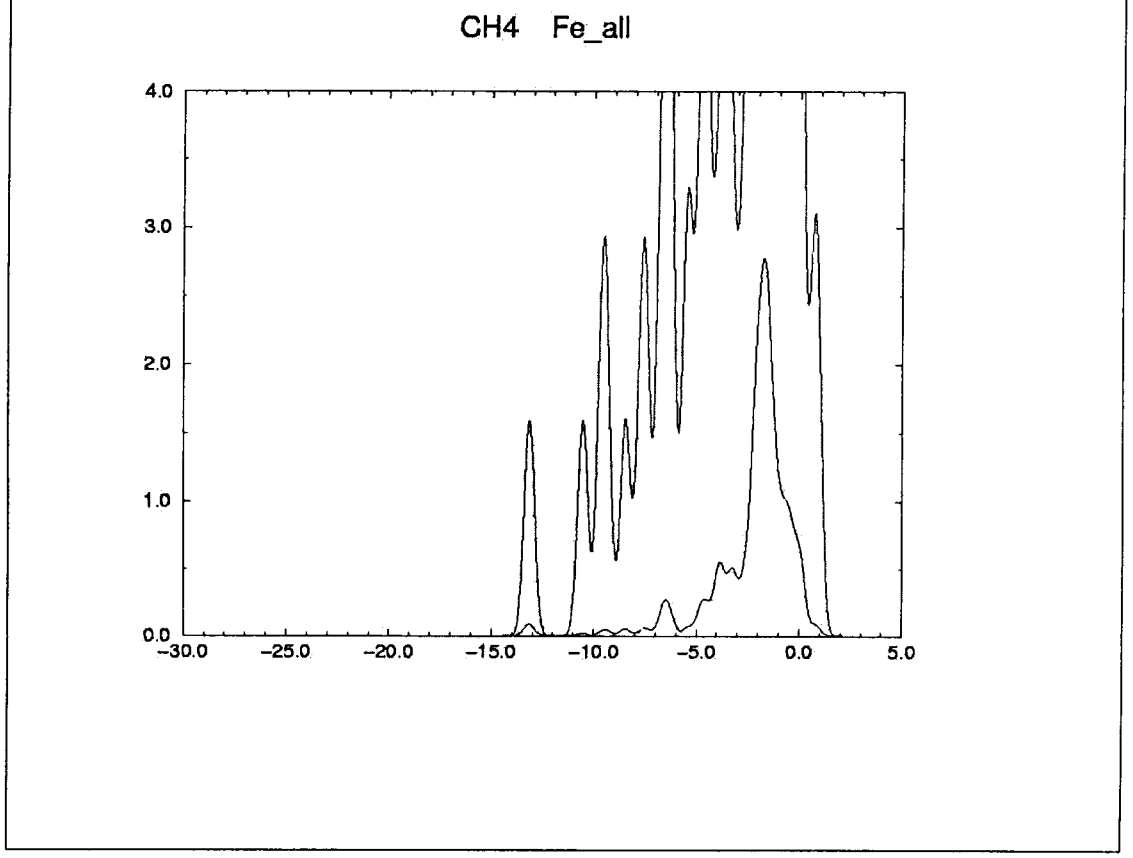


Cerius^2

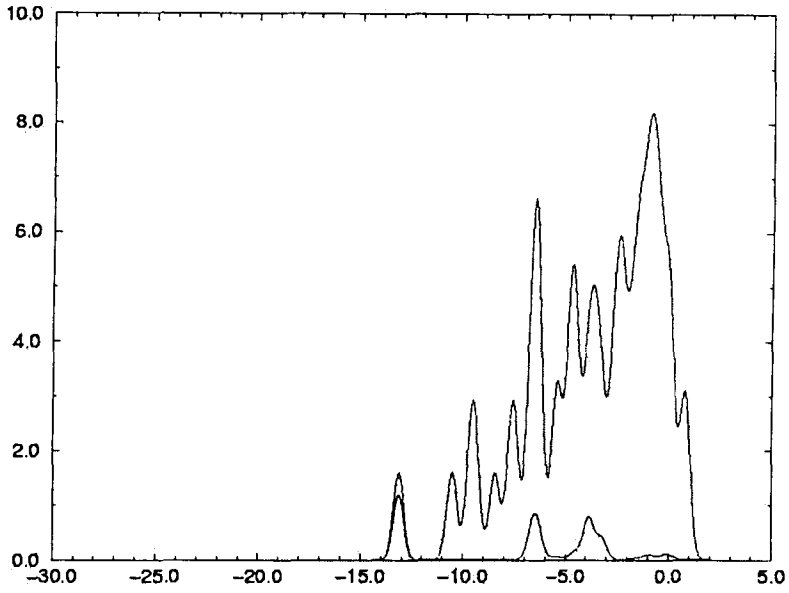
Title:
Author:
Date: Wed Sep 22 15:19:28 1999



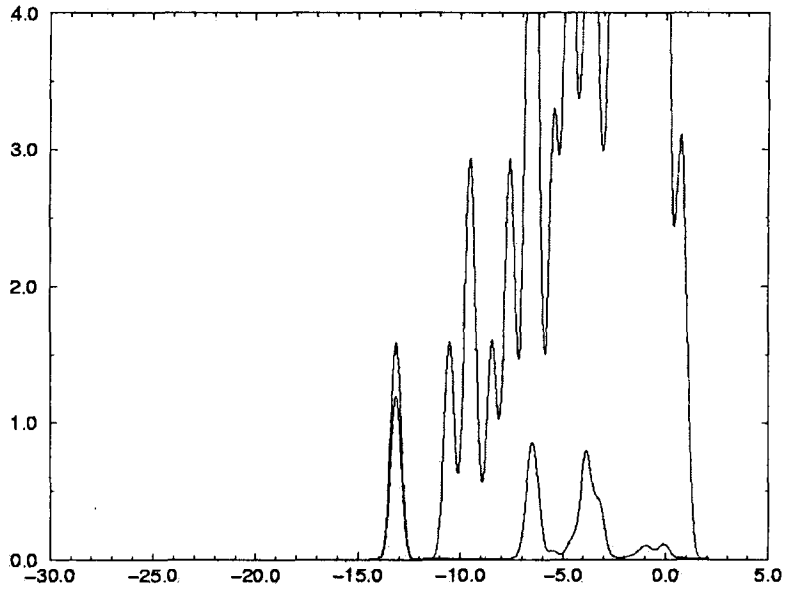

CH4 Fe_all
10.0
8.0
6.0
4.0
2.0
0.0
-30.0
-25.0
-20.0
-15.0
-10.0
-5.0
0.0
5.0


CH4 Fe_all
4.0
3.0
2.0
1.0
0.0
-30.0
-25.0
-20.0
-15.0
-10.0
-5.0
0.0
5.0

CH4 C_all



CH4 C_all



以下三頁中

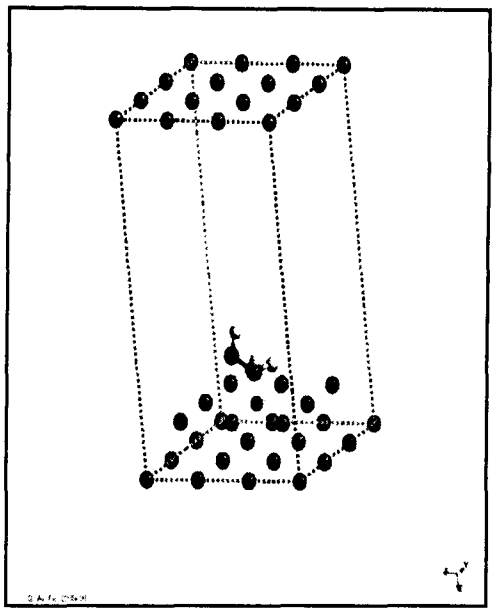
第一頁右上爲脫氫 CH3O 分子吸附在鋁表面，但注意的是鋁表面其中一個鋁改換爲鐵。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的碳與表面的鐵之間的鍵結。也可從等密面圖中看到。

第二頁爲表面鐵的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

第三頁爲脫氫分子中碳的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

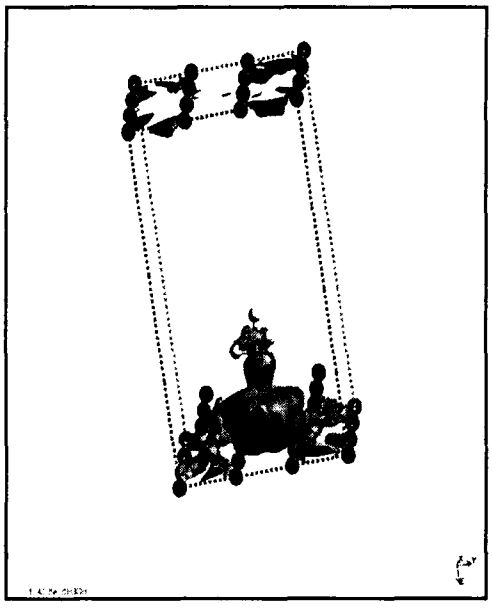
Cerius²

Title:
Author:
Date: Mon Sep 20 08:26:28 1999



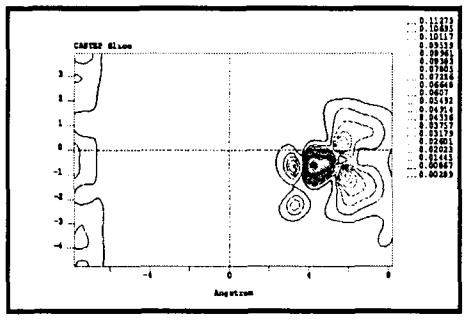
Cerius²

Title:
Author:
Date: Wed Sep 22 20:56:21 1999

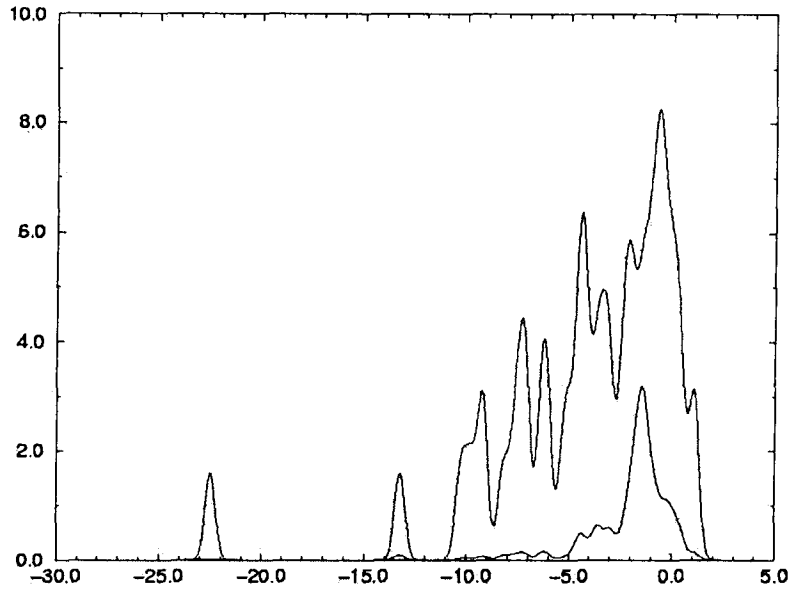


Cerius²

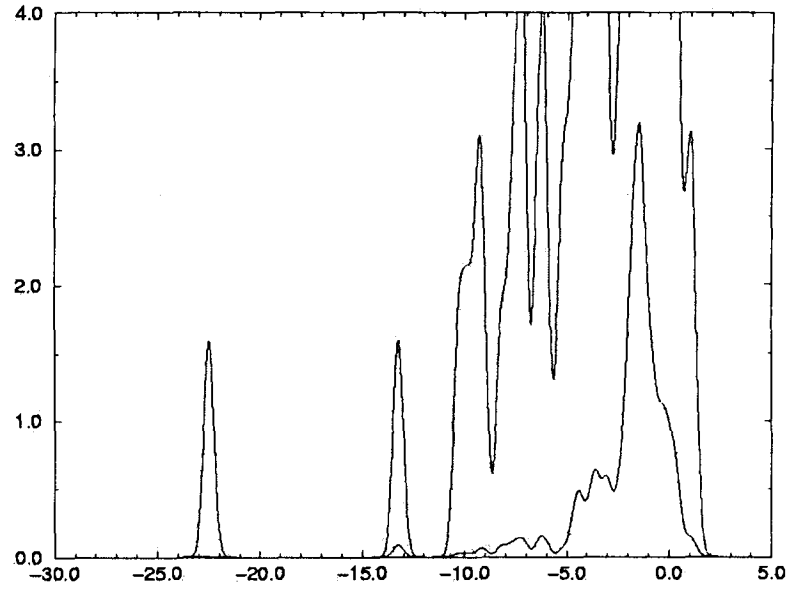
Title:
Author:
Date: Wed Sep 22 20:54:40 1999



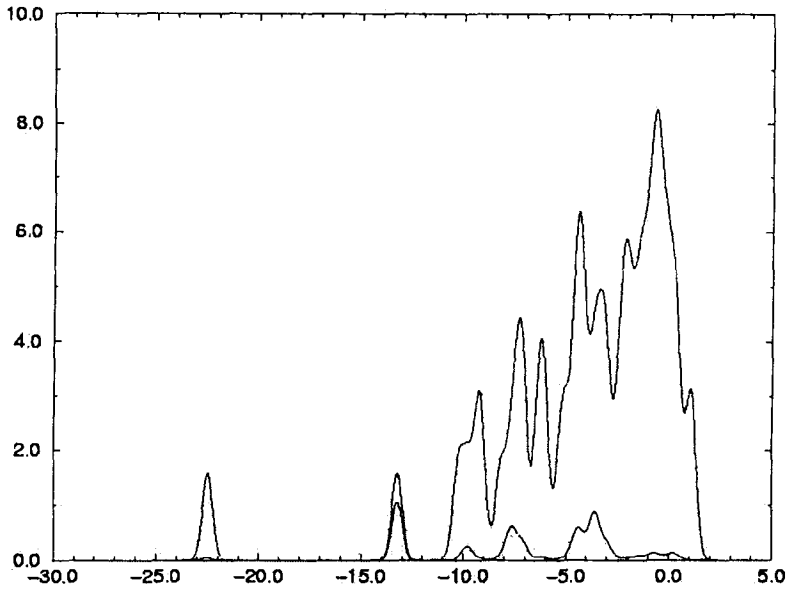
CH3OH Fe_all



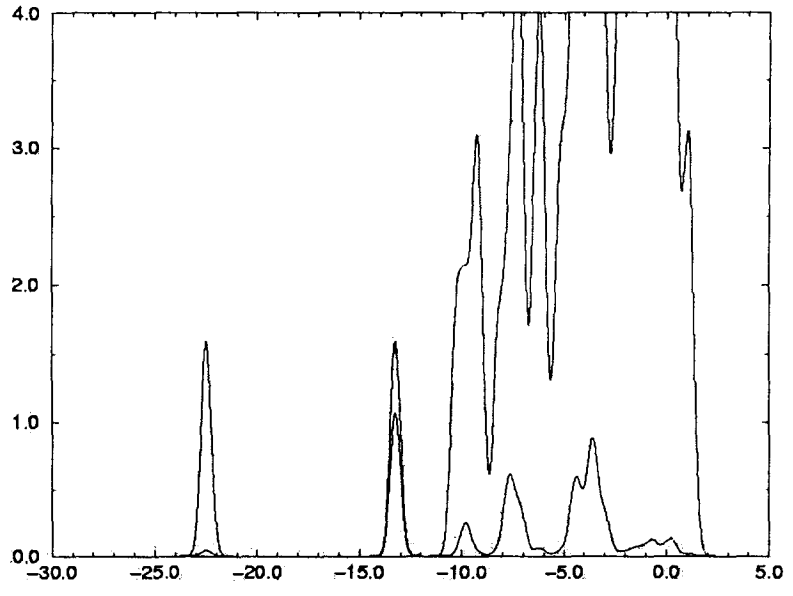
CH3OH Fe_all



CH3OH C_all



CH3OH C_all



以下四頁中

第一頁右上爲脫氫分子 HCOO 吸附在鋁表面，但注意的是鋁表面其中一個鋁改換爲鐵。左下是 orbital density 等密面的圖，可很明顯地看到電子軌域的形狀；右下是此剖面圖，由此密度等高線圖可看出脫氫分子的氧與表面的鐵之間的鍵結爲 antibonding。也可從等密面中看到。

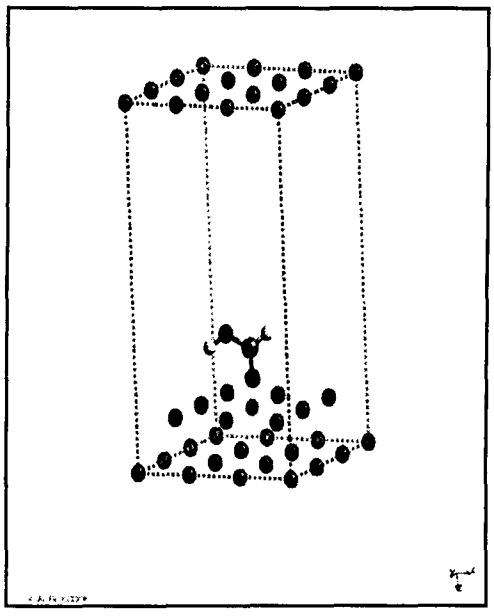
第二頁右上是 total density 等密面的圖，可很明顯地看到電子軌域的形狀；右上是此剖面圖，提供與前兩圖作參考。

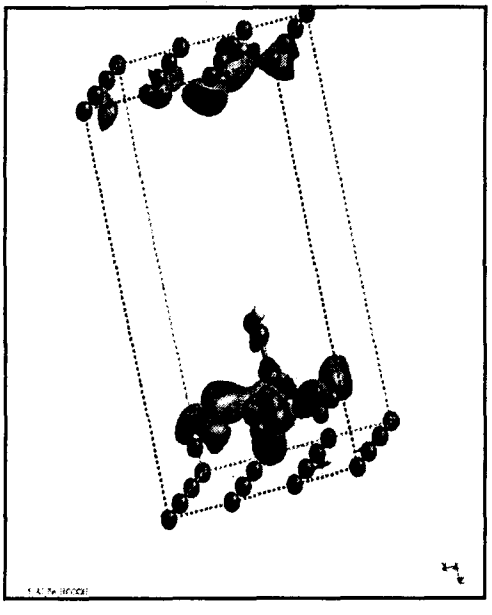
第三頁爲表面鐵的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較

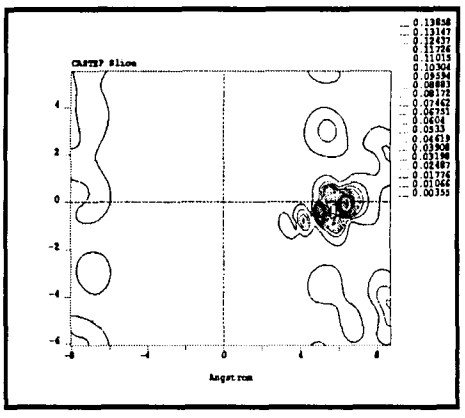
第四頁爲脫氫分子中氧的 PDOS 圖，下圖爲上圖之放大圖，以利觀察比較。

Cerius[2]

Title:
Author:
Date: Mon Sep 20 08:36:08 1999

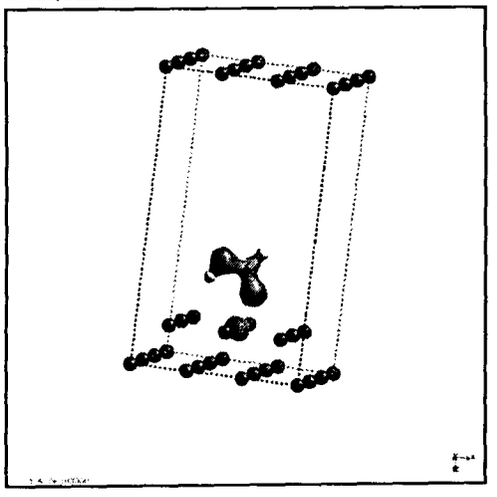






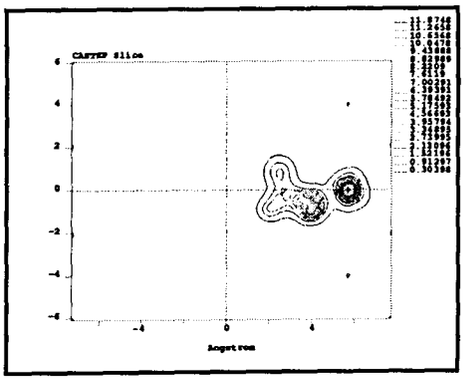
Cerius^2

Title:
Author:
Date: Wed Sep 22 22:36:36 1999

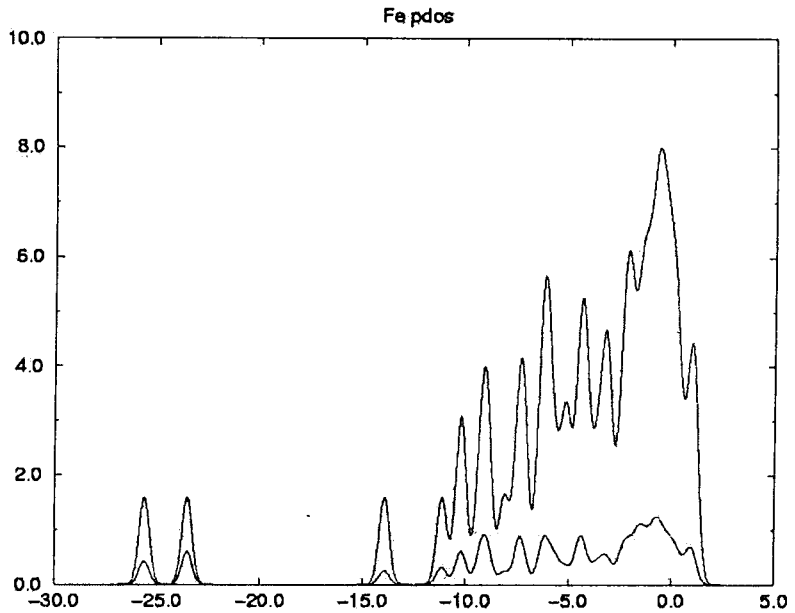


Cerius^2

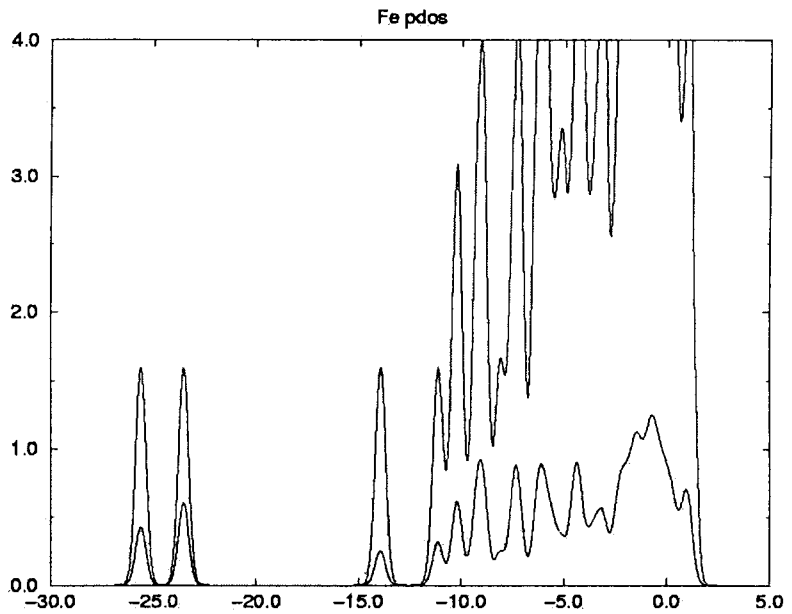
Title:
Author:
Date: Wed Sep 22 22:37:07 1999



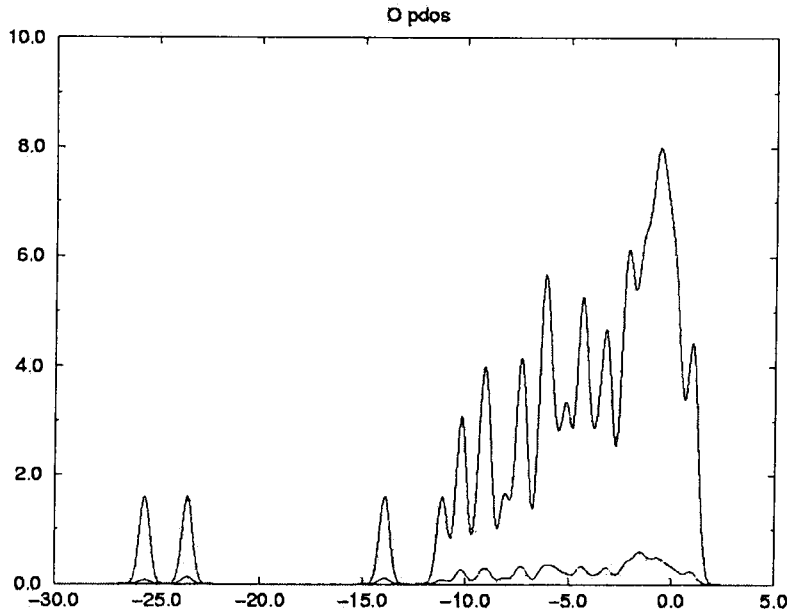
HCOOH Al surface replace one Fe



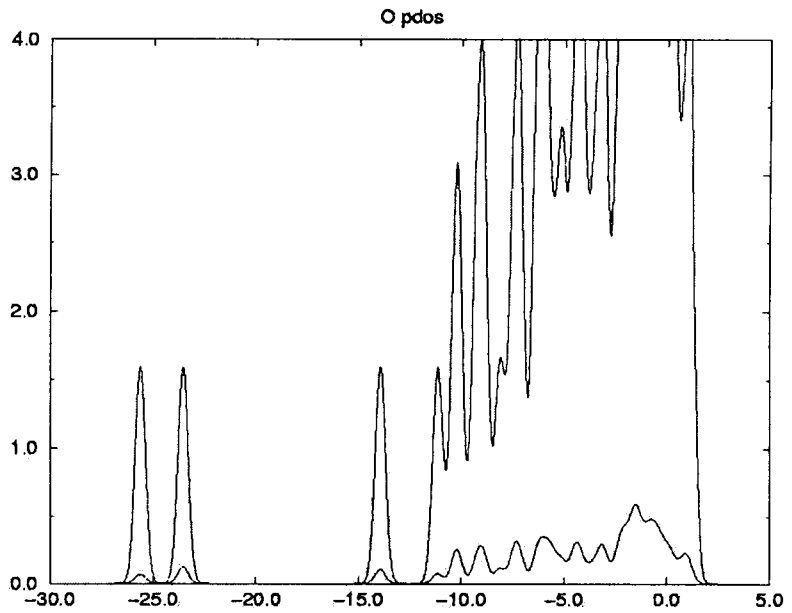
HCOOH Al surface replace one Fe



HCOOH Al surface replace one Fe



HCOOH Al surface replace one Fe



分子片段對金屬表面吸附能之計算方法：

一個中性的分子片段因距離逐漸靠近金屬表面而形成吸附的過程，其吸附能之精確的表示法應爲：

ΔE = E（完整自由分子）＋ E（乾淨表面）－ E（脫氫分子與氫共吸附於表面）

然而，等號右手邊之第三項若要求得系統總能，要在一個模型之內進行金屬表面同時有脫氫分子與氫皆分別鍵結於其上的共吸附計算，其模擬範圍大、原子數多、複雜度亦較高，這樣的計算代價比較大。在此採取一個巧妙的簡化方法；

讓我們考慮在只有氫吸附之金屬表面上，氫原子的去吸附能可表爲：

ΔE1 = E（氫原子）＋ E（乾淨表面）－ E（氫原子吸附於表面）

而對於有脫氫分子與氫原子皆分別鍵結於表面上的共吸附，其氫原子的去吸附能則表爲：

ΔE2 = E（氫原子）＋ E（脫氫分子吸附於表面）－E（脫氫分子與氫共吸附於表面）

一個頗合理的假設是，由於吸附的氫原子很小，離與其一起吸附在表面上的脫氫分子有一段距離，因此互相影響不大。如此，則氫原子的去吸附能 ΔE1 和 ΔE2 將近乎相等，即

ΔE1 ～ ΔE2
由此可推得

－E（脫氫分子與氫共吸附於表面）=
E（乾淨表面）－ E（氫原子吸附於表面）－ E（脫氫分子吸附於表面）

此式中等號右邊的三項都不需要共吸附計算便可以求得，而其結果恰可代回用於求得真正的吸附能 ΔE ，而整個過程都不必再有大範圍共吸附的複雜計算。本研究案中的一系列吸附能，即是此種方法獲得。當然，爲了驗證此一假設的適用性，我們針對 CH4/鋁 及 H3PO4/鋁 分別做了較複雜的共吸附能計算，求得之結果與近似法比較，其一致程度令人滿意，不會影響定性上的探討。

各種鍵能及吸附能的表列可如下：

兩層鋁乾淨表面截止能量測試結果

截止能量	能量(eV)
60	-1009.4569441
110	-1016
160	-1018.9002471
210	-1019.4669567
260	-1019.5883765

兩層鋁-鐵乾淨表面能量

截止能量	能量(eV)
240	-1828.8722968

四層鋁表面能量分析

E_CUT (截止能量)	能量(Ev)
60	-1805.9530225
260	-1824.8842091

獨立脫氫分子能量分析

脫氫分子	能量(eV)
CH3	-201.1501149
HCOO	-1044.3221880
H2PO4	-1964.2885481
CH3O	-639.3544870

獨立分子能量分析(完整分子)

完整分子	能量(eV)
CH4	-219.2096035
HCOOH	-1062.4332188
H3PO4	-1982.3614739
CH3OH	-657.1439

脫氫分子吸附在二層鋁表面的能量分析

吸附鋁表面的脫氫分子	能量(eV)
CH3	-1222.6525749
HCOO	-2082.7055163
H2PO4	-2987.8660308
CH3O	-1660.7081890

脫氫分子吸附在二層鋁-鐵表面的能量分析

吸附鋁-鐵表面的脫氫分子	能量(eV)
CH3	-2032.8215855
HCOO	-2893.0080340
H2PO4	-3797.2996803
CH3O	-2470.9480523

脫氫分子吸附在四層鋁表面的能量分析

吸附鋁表面的脫氫分子	能量(eV)
CH3	-2027.5667701
HCOO	-2872.4837095

吸附鋁表面之鍵能值　　對鋁表面之吸附能

脫氫分子	鍵能(eV)	完整分子	直接模擬吸附能(eV)	吸附能(eV)
CH3	1.9140835	CH4	-0.3336	-0.288
HCOO	0.683921	HCOOH	0.683921	0.683921
H2PO4	3.9891062	H3PO4	1.782	1.773
CH3O	1.7653255	CH3OH	-0.152	

吸附鋁-鐵表面之鍵能值　　對鋁鐵表面之吸附能

脫氫分子	鍵能(eV)	完整分子	吸附能(eV)
CH4	2.799	CH4	0.329
HCOOH	1.69	HCOOH	1.69
H3PO4	3.863	H3PO4	1.5356
CH3OH	2.718	CH3OH	0.536

從量子態觀察

吸附前和吸附後的確有看到量子態的變化，從態密度的比較圖可以清楚的看出，並了解其能量下降的機制。

我們看到了磷酸根上的氧原子之 s 與 p 軌域在吸附鋁金屬表面後有重新混成的現象，使得 s 成份減少而 p 份增加。這與我們所觀察到之氧原子在吸附到鐵之後所形成的 π 鍵，都代表著氧原子 p 軌域活化而主導吸附的特性。

結論與建議

從能量（吸附能/鍵能）來看：

我們預測 -[C]H2- 與 -O-[C]H2- 在對金屬表面的吸附能力都是負面的，也就是說，這兩類的分子片段在高分子上都沒有吸附到金屬表面上的趨勢。這些分子片段對於吸附是沒有貢獻的。至於 -[C=O]-O- 則不然，該分子片段中 C=O 的氧原子是指到金屬表面上去的。這一個片段不涉及氫的解離（因爲無氫可脫），我們發它的吸附能是 0.68 eV，是一個頗強的化學吸附。更有趣的是，磷酸根進行脫氫吸附的過程時，它所獲得的能量比 C=O 的更大，是 1.73 eV。這解釋了爲什麼環氧樹脂高分子鍊上含有磷酸根時，對於金屬表面的吸附力會增強。至於含鐵之金屬表面的吸附，其趨勢也是一樣指出 -[C]H2- 與 -O-[C]H2- 對吸附現象沒有貢獻，而 -[C=O]-O- 及磷酸根有正面的貢獻。在此由於含鐵部分是一個比較理想化的模型，是用一顆鐵原子植入於鋁表面之中，因此我們對於這部分的數據應有所保留，僅作爲定性上討論的參考。

吸附能/鍵能的相關計算，由於它能夠從量子力學的角度來回答磷酸根對黏著力的影響，在現有計算規模及數據品質、以及配合初步探討目標而言，是成功的。綜合本案所需的計算資源以及材料設計可能獲得的效益，非常值得做下一步更精確計算。

從計算分析後獲得之結果：

在含鐵原子金屬表面的吸附計算，我們看到凡是有氧去接鐵原子的，都有 π 鍵的出現（出現在離費米面 ？eV 的能階位置）。從軌域電荷密度可以清楚的看到，這樣的 π 鍵是由鐵原子貢獻 d 軌域，氧原子貢獻 p 軌域的鍵結所形成的。對於非過渡金屬而言，這樣的特殊鍵結就不可能存在，因爲根本沒有具化學活性的 d 軌域可以參與交互作用。如此一來，磷酸根（其上有氧與金屬相接者）或者隨著金屬種類的不同至少會有兩大類不同的鍵結，至於其強弱關係則需依不同金屬種類個別計算方能預測。此一結果，對於依照待處理之金屬不同而有不一樣之塗料分子設計，是具有潛在價值的一個發現。

缺點檢討：

（一）時間進度掌握

由於本校科學館整修及九二八大地震所造成之多次不正常電力中斷，在計畫開始直到去年夏季期間累積的計算結果全部遭到不可修復之損失，造成必需申請延長計畫，並且所剩的計畫執行時間不足，導致進行計算可用的時間遭到嚴重的壓縮。

（二）表面模型層數太少

由於前述時間壓縮的關係，我們在不得已的情況下，在模型的建構上採取使用較大膽的近似，使用兩個原子層來代表金屬表現的效應。根據以往的經驗，此一舉動無可避免地會降低能量計算值的準確性。所幸我們在本研究案中的現階段只希望得到鍵能變化的趨勢，而不一定要極準確的計算。除了模型的層數較少之外，所有其他的計算參數我們都遵循保守而精確的設定值。

總結：

本研究案的計算結果雖然是來自於一個相對簡化的模型預設之下，其成果卻有以下兩層意義，首先是闡明量子力學在此類科技應用及分子設計的用法，並且成功地解釋了實驗觀察到的現象。本案中所有我們所使用的方法及依循的步驟，都有學術上已經成熟且穩定的技術可以運用，因此雖然設定於計算量較小的研究較小，但方法本身卻完全沒有大小的限制。透過本案研究作爲一種個案示範，符含應用技術開發及技術轉移之精神與利益，亦即將學術成果推廣於工業界。其次，本案簡單化的模型設定呈現了結果的明確性，突顯兩種極端不同之金屬類別在被含磷酸根環氧樹脂吸附下的共同性與相異性。

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仲琦公司〔MSI Cerius2 CASTEP 之台灣代理〕提供 CASTEP 資料

國家高速電腦中心之計算機時間

淡江大學化學系陳幹男教授

淡江大學化學系林志興教授

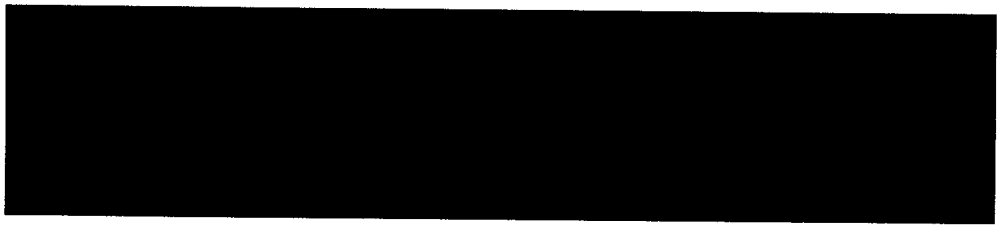
資料

摘錄自 Cerius2 手冊，感謝 MSI 惠允引用

CASTEP 基本原理

CASTEP 計算方法

CASTEP 操作範例



3 General Theory

Introduction

Chemists working with large and small molecules are accustomed to using computer codes and software modules that are based on quantum mechanical methods. But most properties of macroscopic materials depend on microscopic phenomena to one degree or another and also require for their correct description the application of quantum mechanics. In some cases, such as optical or magnetic properties, this is particularly obvious and direct. In other cases the link is less direct, but still very important. For example the density of a bulk solid is determined to a large extent by the forces that operate between neighboring atoms. As in a molecule, the equilibrium geometry, which ultimately determines the density, is a consequence of a balance of forces mediated by the electrons, which obey quantum mechanics. In a pure crystalline solid, the macroscopic density is determined uniquely by the size of the unit cell and the mass of the atoms it contains. In a mixture, or polycrystal, the density is determined by a weighted average of the densities of the constituent crystalline phases. Thus even an obviously macroscopic materials quantity such as the density is a *quantum property.*

Over the past four decades, our ability to treat materials properties at a fundamental, quantum level has improved tremendously, in large part because the advance of computer power has allowed us to actually solve hard equations and try things out. Today it is possible, for instance, to calculate the unit cell dimensions of a crystalline solid from first principles with a reliability in the range of a few percent. A wide variety of geometric and structural behavior, such as the location of impurities, the structure of defects, dislocations, grain boundaries, surfaces can similarly be calculated from first principles. Once the geometry has been determined, a range of properties, electronic optical and magnetic can also be calculated with varying degrees of reliability.

The advances that made this possible were largely incremental and are described in various contexts in terms of *one-electron theory*, *band theory* or *self-consistent-field theory*. From the late 1960s onwards, these terms found some formal legitimacy in a theory of energy and force in electronic systems called *density functional theory*. Today, most quantum applications with a legitimate claim to being "materials specific" are justified in terms of formal density functional theory. This is not always entirely a simple matter and there remain some formal and technical issues, but the pragmatic person interested more in the result than the manner at which it is arrived at need not be too concerned with technical caveats. The theory underlying all the modules from MSI's quantum suite is underpinned in one way or another by the equations of density functional theory.

Density functional theory

The existence of *correlations* between the particles, the main formal difficulty encountered in treating a materials problem in quantum mechanics, is a familiar one in many contexts. The positions and motions of the particles that make up a molecule or material are correlated because the particles interact with each other and exert forces upon each other as they move. In quantum mechanics, the situation is further compounded by the mysterious forces that devolve from the Pauli exclusion principle governing electrons. This causes correlations to appear even between (fictitious) noninteracting particles that have no direct interaction with each other. Such forces are referred to as *exchange forces* because they have to do with the set of rules in quantum mechanics that govern what happens when the labels characterizing indistinguishable particles are exchanged.

Whether due to interactions (e.g., the Coulomb force) or exchange, correlations can be characterized as either long- or short-range. The former can be dealt with by averaging techniques and a *mean-field* or a *self-consistent field* (meaning that the field experienced by an atom depends on the global distribution of atoms). Short-range correlations involve the local environment around a particular atom, i.e., deviations of the local environment from average behavior, and are much more difficult to treat. In large part, the central problem of quantum methods in chemistry and condensed matter physics has been the search for more and more accurate ways of incorporating short-range correlations into mean-field theory. The massive cpu requirement of codes that employ modern methods such as *coupled clusters* or *Quantum Monte Carlo* bear witness to the degree of difficulty of the problem. These methods are applicable only to relatively small molecules or very simple crystalline solids and their scaling properties as the system size increases are very unfavorable.

Fortunately, the fine details of short range correlations are often of only minor importance so that a theory based on the concept of a mean or self-consistent field is sufficiently accurate for many purposes. Where this is not the case, as in the high temperature ceramic superconductors, or *valence-mixed* solids, one refers to *strongly correlated systems*, implying that the short-range correlations between electrons due to exchange and their mutual Coulomb repulsions must be accounted for very accurately if even the qualitative features of observed behavior are to be reproduced.

Several promising methods of dealing with the problem of *strong correlations* have been developed in recent years but this is still at the cutting edge of research in condensed matter physics and none of these methods is quite ripe for inclusion in a suite a general software tools. An important advance in the calculation of the energy of collections of atoms and the forces on each atom was made by Kohn and Sham (1965), who showed how a mean-field theory could be applied to this problem. In their method, the electron density plays a crucial role so that, although the term has more general applicability, the Kohn-Sham method is commonly referred to as *density functional theory*. This has since advanced to become a very important method for determining the energy of many-electron, and therefore many-atom systems. In addition, Kohn-Sham density functional theory is equally applicable to molecules (bounded collections of atoms) and crystalline materials (where a specific unit cell is repeated throughout space).

In density functional theory, the energy is not written in terms of the many-electron wavefunction as is conventional in quantum chemistry, but as a functional of the electron density. Kohn and Sham proposed that the functional for a system of electrons with external field $V_{ext}(x)$ be written in the form

Eq. 1 $$E_{ks}[\rho(x)] = T_s[\rho(x)] + E_{es}[\rho(x)] + E_{xc}[\rho(x)] + E_{ext}[\rho(x)]$$

where the terms refer to the kinetic energy of non-interacting electrons having density $\rho(x)$, the electrostatic energy, the so-called exchange-correlation energy, and the potential energy of non-interacting electrons having density $\rho(x)$ in the external field $V_{ext}(x)$. The important advance of Kohn and Sham was the correction of a defect of earlier forms for the density functional (such as the Thomas-Fermi-Dirac functional) with regard to reproducing the shell structure of atoms. This is achieved in the Kohn-Sham functional via the kinetic energy term which is expressed by a set of orbitals, ϕ_n, emanating from a one-particle Schr錸inger equation;

$$T_s[\rho(x)] = \sum_{\alpha} a_{\alpha} \int dx\, \phi_{\alpha}(x) \left\{ -\frac{\hbar^2 \nabla^2}{2m} \right\} \phi_{\alpha}(x)$$

Eq. 2

The link between T_s and $\rho(x)$ is then indirect, via the orbitals, ϕ_n, in terms of which

$$\rho(x) = \sum_{\alpha} a_{\alpha} \left| \phi_{\alpha}(x) \right|^2$$

Eq. 3

Here the a_n are occupation numbers that determine the electron configuration. $T_s[\rho(x)]$ and $\rho(x)$, as given by Eq. 2 and Eq. 3, provide the required link between a density and the kinetic energy with which it is associated.

For purposes of practical calculation, the Kohn-Sham functional must be supplemented by an approximation for the exchange and correlation term. The traditional approximation, proposed by Kohn and Sham, is referred to as the "local density approximation" (LDA) and takes the form

$$E_{xc}^{h}[\rho(x)] = \int dx\, \rho(x)\ \varepsilon_{xc}^{h}(\rho(x))$$

Eq. 4

where $\varepsilon_{xc}^{h}(\rho)$ is the exchange correlation energy of a homogeneous electron gas having density ρ. Although this form of the exchange correlation energy appears to be valid only in the limit that the electron density is slowly varying (in which case Eq. 4 is the first term in a gradient expansion), a posteriori calculation showed that the expression remains relatively accurate in general, even when the density is so rapidly varying that a gradient expansion of it does not exist. Arguments of a dimensional nature having nothing to do with gradient expansions help to explain the general accuracy of Eq. 4 and suggest why this expression gives a reasonable estimate of the exchange-correlation energy irrespective of the nature of the density distribution. The quantity $\varepsilon_{xc}^{h}(\rho)$ has been calculated in several ways by different groups. The calculations give similar, but not identical results. The differences to be expected on switching from one LDA functional to another are, in general, only marginal.

The LDA remained the approximation of choice for E_{xc} for many years (and is still for some applications, particularly in extended systems). In applications to molecules, however, it was found that the LDA tends to overbinding (too large values of molecular binding energies). This can be understood as a consequence of a known defect of Eq. 4. In regions of low electron density. Here, the exact form of ε_{xc}^{h} is known (it is some kind of electrostatic interaction having the functional form of a power law) and deviates greatly from the LDA which falls off exponentially with the electron density. This means that the exchange correlation contribution emanating from regions of low electron density is underestimated, which, in turn, implies that the difference in energy between two systems whose electron distributions have different "surface areas" will be in error. This is the case when two atoms combine to form a molecule and the sign of the effect is consistent with overbinding of the molecule.

Over the past decade, a class of corrections to the LDA has been developed that correct this deficit to a large extent by going over explicitly to the power law form in regions of low density. This is usually done by introducing a dependence on the gradient of the density and the new class of corrected exchange-correlation functionals is referred to as *gradient corrected* or *Generalized Gradient Approximations* (GGA). The use of gradient corrections has little influence on local properties such as bond lengths or vibration frequencies, but does lead usually to a significant improvement in global changes in the energy such as those that result when two atoms form to make a molecule, or a molecule binds on a surface. The hunt for yet further improvement in exchange-correlation functionals continues, though this is unsystematic and there is no guarantee that higher accuracy can be attained than is already exhibited by the functionals commonly in use

today.

The energy of a system of electrons in an external field (such as that due to a collection of nuclei) is given by minimizing the density functional Eq. 1. This is equivalent to solving a set of Kohn- Sham equations comprising a one-particle Schr錄inger equation together with a so-called self-consistency condition. The Schr錄inger equation links the input potential to the output density of the Schr錄inger equation:

Eq. 5a $$\{-\frac{\nabla^2}{2m} + V_{eff}(x) - \varepsilon_n\}\phi_n(x) = 0$$

Eq. 5b $$V_{eff}(x) = V_{ext}(x) + \Phi(\rho(x)) + \mu_{xc}(\rho(x))$$

where Φ is the Coulomb potential corresponding to $\rho(x)$,

Eq. 6 $$\mu_{xc}(\rho) \equiv \frac{d}{d\rho}\left[\rho\varepsilon_{xc}^{h}(\rho)\right]$$

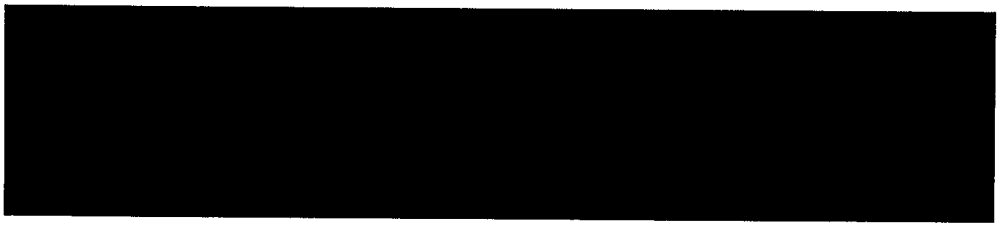
and the output density, $\rho(x)$, is given in terms of the orbitals by Eq. 3. Eq. 5a and Eq. 5b are usually solved by iteration. Beginning with a start potential, equation Eq. 5a is solved and its *out* density calculated from the orbitals via Eq. 3. Then this density is used to form a new potential for equation Eq. 5a. The self-consistency cycle is then continued until the *in* potential and the out-density satisfy Eq. 5b to some desired accuracy. This often involves many iterations because the self-consistency procedure is inherently unstable. Sophisticated "feedback" techniques are necessary to prevent oscillations.

Once self-consistency is achieved, the calculational output includes the energy, Eq. 1, it's derivatives with respect to the nuclear coordinates (i.e., the atomic forces), the eigenvalues of Eq. 5a (which in extended systems give the energy bands), and the one electron orbitals $\rho(x)$. According to formal density functional theory, only the energy and its derivatives (the forces on the ions) have physical significance. However, practical calculation over many decades has shown that many other quantities, calculated approximately in a "one-electron picture" using the eigenvalues (energy bands) and orbitals or Eq. 5a, are given with equal accuracy. These include (in many cases) the optical absorption, which is treated by assuming the electrons of the system to be excited from occupied to unoccupied levels as the result of photon absorption, and the magnetic structure of materials. This is calculated using a spin-polarized version of the theory in which the electrons of up-spin and down-spin may experience different potentials. It is then possible for the system to adopt a *symmetry broken* configuration wherein there is a preponderance of one kind of spin and therefore a magnetic state. The use of the local spin-density approximation for the exchange correlation energy, which is analogous to Eq. 4. but with allowance for different densities for up- and down-spins, gives surprisingly accurate data for the magnetic structure of metals and alloys. Spin-polarized calculations are also important in dealing with open-shell atoms and molecules.

In short, the solution of the Kohn-Sham equations, Eq. 5a and Eq. 5b, for a collection of atoms, whether in a molecule, cluster or extended solid provides a wealth of information about the system. This includes structural information, such as the equilibrium geometry, and a wide variety of important electronic properties. In addition, dynamical and thermal behavior can be studied using forces generated by the solution of the Kohn-Sham equation in, e.g., molecular dynamics calculations (so-called *ab-initio molecular dynamics*). Although Eqs. 5 are very much simpler than standard quantum mechanics -- because the Coulomb interaction is treated via a mean-field -- this does not mean that they can be easily solved. The functional dependence of the exchange correlation energy density on the electron density is non analytic, so exact, analytic solutions are not possible even for the hydrogen atom. Methods yielding numerically exact solutions are possible, but only for very small systems (atoms and small, light molecules). In general, approximate methods must be used. Over the years, a number of standard methods have been applied with varying degrees of success. Each has strengths and weaknesses in terms of the systems and/or properties for which it is most accurate.

Each of quantum modules (CASTEP, ESOCS, and FastStructure) involves the solution of Eqs 5. in one guise or another. The modules differ from each other in the method employed and the kinds of systems and properties for which this is particularly appropriate, and they exhibit complementary strengths. A specific, well-posed problem is usually best addressed by one specific module which will yield either the most accurate, or the fastest solution to the problem (or both). For example, the atoms in semiconducting materials can usually be represented by weak pseudopotentials for which methods involving plane wave expansions are particularly appropriate. Accordingly, problems in semiconductors are usually best addressed using CASTEP, which employs plane wave technology. For most metals applications, the code of choice would be ESOCS (Electronic Structure of Close-packed Solids). Note, however, that ESOCS does not allow geometry optimization, and will not work for metal surfaces.

In more extensive studies, a problem is best solved using a combination of modules. A large-scale structural or dynamical study, for example, is best carried out by using initially the module MOPAC (molecules) or FastStructure, which performs geometry optimizations, simulated annealing and molecular dynamics on molecules or solids. Once the basic behavior of the system has been determined, refinement of the results and properties of the system in its equilibrium configuration can then be determined using DMol or ADF or ZINDO (molecules) or CASTEP or ESOCS (solids).



4 CASTEP

Introduction

The CASTEP module provides a comprehensive, easy-to-use interface to the CASTEP/CETEP computational physics/chemistry programs. This interface allows you to utilize the intuitive GUI and modeling environment provided by the Cerius² Visualizer to efficiently exploit the quantum mechanical functionality of CASTEP.

Note

Although CASTEP is primarily intended for use on large-scale periodic systems, it can also be applied to supercells constructed to study defects, surfaces/interfaces, and molecules. For more information about studying these, see "Nonperiodic systems" on page 42.

The CASTEP module allows you to use the flexible molecular modeling tools and advanced GUI provided by the Cerius² modeling environment to generate and specify models for study, define the type of job you want to perform, and run it on your local machine or a remote host.

Upon completion of your CASTEP run, you can use the CASTEP module's analysis tools to extract and visualize data from the raw output produced by CASTEP. The raw output describes the properties of your model in terms of numerous sets of numbers.

Interface mechanism

Although the mechanism is largely transparent, Cerius² interfaces with CASTEP through several CASTEP input and output datafiles created by the user interface. The options you set that define the job to be run and the model on which it is to be performed are all used to create a file that is then passed to CASTEP as input.

If the CASTEP run completes successfully, the results are written to output files. The CASTEP module's analysis tools read these output files, extracting and correlating more readily useful information from the raw data output.

CASTEP theory

The CASTEP package is capable of simulating electronic relaxation to ground state for metals, insulators, or semiconductors. Using these techniques, CASTEP can calculate forces acting on atoms and stress on the unit cell. Atomic forces can be used to find the equilibrium structure or to perform molecular dynamics simulation (with canonical or microcanonical ensemble).

Introduction

The theoretical basis of CASTEP is the density functional theory (DFT) in the local density approximation (LDA) or gradient-corrected LDA version, as developed by Perdew and Wang (GGA). The DFT description of electron gas interactions is known to be sufficiently accurate in most cases, and it remains the only practical way of analyzing periodic systems. For a more complete description of DFT, see Chapter 3.., *General Theory*.

The default setting in CASTEP is GGA, which is known to be a superior method in many cases. Gradient corrected method is more accurate in studies of processes on surfaces, of properties of small molecules, hydrogen-bonded crystals, crystals with internal surfaces (zeolites). LDA is known to underestimate bond lengths in molecules and cell parameters in crystals, while GGA typically remedies this shortcoming. However, there is much evidence that GGA is prone to overcorrect the LDA result in ionic crystals; it often overestimates cell parameters when LDA data is in good agreement with experiment. It is thus difficult to recommend one specific method as the best approach for all systems.

Pseudopotentials

The electron-ion interaction is described using a *pseudopotential* concept. For each element, CASTEP provides a selection of potentials:

Potential	Filename extension
ultrasoft	.usp
norm-conserving potential generated using the optimization scheme of Lin et al.	.recpot
norm-conserving potential generated using the optimization scheme of Troullier-Martins	.pspnc
non-optimized hard norm-conserving potential generated using the Teter scheme	.psp

The methodology of norm-conserving potentials is quite well-known and extensively validated. In such a scheme, the pseudo-wave-function matches the all-electron wave function beyond a cutoff radius that defines the core region. Within the core region, the pseudo-wave-function has no nodes and is related to the all-electron wave function by the norm-conservation condition: that is, both wave functions carry the same charge. These potentials can be made very accurate at the price of having to use a very high energy cutoff. Teter potentials represent an example of such accurate, but extremely hard, pseudopotentials. The optimized schemes, in particularly the scheme of Lin et al., allow one to generate soft norm-conserving potentials. However, the energy cutoff needed to describe the localized valence orbitals of first-row elements (C, O, N) or transition metals (Ni, Cu, Pd) is still frequently too high.

The idea of ultrasoft pseudopotentials (USP) as put forward by Vanderbilt is that the relaxation of the norm-conserving condition can be used to generate much softer potentials. In this scheme the pseudo-wave-functions are allowed to be as soft as possible within the core region, so that the cutoff energy can be reduced dramatically. Technically, this is achieved by introducing a generalized orthonormality condition. The electron density given by the squared moduli of the wave functions has to be augmented in the core region in order to recover the full electronic charge. The electron density is thus subdivided into (1) a smooth part that extends throughout the unit cell, and (2) a hard part localized in the core regions. The augmented part appears in the density only, not in the

wavefunctions. This differs from methods like LAPW, where a similar approach is applied to wavefunctions.

Ultrasoft potentials have another advantage besides being much softer than the norm-conserving potentials. The USP generation algorithm guarantees good scattering properties over a pre-specified energy range, which results in much better transferability and accuracy of pseudopotentials. USP usually also treats "shallow" core states as valence by including multiple sets of occupied states in each angular momentum channel. This also adds to high accuracy and transferability of the potentials, although at a price of computational efficiency.

The default potentials used by CASTEP are ultrasoft pseudopotentials.

All pseudopotentials are used in a separable Kleinman-Bylander form. Norm-conserving potentials can be applied to wavefunctions in either reciprocal or real space; the real space implementation offers better scalability with system size. Ultrasoft potentials can be used only in the reciprocal space at the moment (note that the expected gain of the real-space implementation is expected to be less important in this case).

At present CASTEP pseudopotentials are available for all elements of the periodic table. However, USP files are not provided at the moment for f-elements, with few exceptions, so that one must use .pspnc files instead.

Supercell approach

CASTEP is based on a supercell method, whereby all studies must be performed on a periodic system, even when the periodicity is superficial. For example, a crystal surface must be represented by a finite-length slab. Study of molecules is also possible by assuming a molecule is put in a box and treated as a periodic system. There is no limitation on the shape of the supercell. If the crystal possesses high point-group symmetry, it can be used to speed the calculations.

Electronic relaxation

CASTEP offers a choice of methods for electronic relaxation. The default method is the most efficient and is based on density mixing (see Kresse et al.). In this scheme the sum of electronic eigenvalues is minimized in the fixed potential instead of self-consistent minimization of the total energy. The new charge density at the end of the step is mixed with the initial density and the process is repeated until convergence. A number of options are supported for this scheme: linear mixing, Kerker mixing and Pulay mixing, in order of increasing robustness. It is possible to use either the conjugate-gradient based approach to minimize the sum of eigenvalues, or the residual minimization method which uses the DIIS (direct iteration in the inverse subspace) scheme. A slightly more elaborate scheme that involves separate mixing of spin density has been developed for spin-polarized calculations.

CASTEP also supports a more traditional scheme of the electronic relaxation, involving minimization of the total energy. The electronic wave functions are expanded using a plane-wave basis set, and the expansion coefficients are varied so as to minimize the total energy. This minimization can be achieved either by using a band-by-band technique, where each wavefunction is optimized independently, or by a modern all-bands method that allows simultaneous update of all wavefunctions (only the all-bands scheme is supported for ultrasoft potentials). The scheme uses a preconditioned conjugate gradients technique, as described by Payne et al.

The main advantage of the density mixing method is its robustness for metallic systems, especially for metallic surfaces. A traditional total energy minimization scheme might become unstable in a metallic system with the cell elongated in one dimension, and this is the typical set-up for the supercell calculations on surfaces. The density mixing scheme converges equally well for insulating and metallic cases.

Other technology used

CASTEP uses special k-points sampling for integration over the Brillouin zone, fast Fourier transforms (FFT) to evaluate matrix elements, and wavefunction symmetrization for crystals with

point-group symmetry higher than P_1. For metallic systems CASTEP introduces partial occupancies for levels close to the Fermi energy (de Vita, 1992).

Major limitations

CASTEP suffers from all the typical problems associated with local density approximation (or more generally with the use of density functional theory). For example, the band gap in insulators is underestimated and one has to apply post-SCF corrections (scissors operator) to achieve agreement between measured and calculated optical properties.

Applications and further references

The range of CASTEP applications in total energy modeling and electronic structure study is reflected by the number of related research papers published in peer-reviewed journals each year. Some representative examples are cited in the References appendix. In addition, there is an online list of CASTEP publications at

http://www.msi.com/info/references/CASTEP_list/CASTEP_pubs.html

The finite basis set correction

The finite basis set correction is of utmost importance when cell optimization is performed with a basis set that is not absolutely converged. For example, the silicon pseudopotential is sufficiently soft and provides fairly accurate results with a cutoff energy for plane waves of about 200 eV. However, if one calculates the equation of state using this cutoff (i.e., the volume dependence of the total energy and pressure), the volume that corresponds to the minimum in total energy does not coincide with the volume that gives zero pressure. As one repeats such EOS calculations at progressively higher cutoff energies and with better k-point sampling, the difference between the two volume values becomes smaller and smaller. In addition, the E-V curve calculated at low cutoff energy is jagged but becomes more and more smooth as the cutoff energy is increased.

The idea behind the finite basis set correction is to use results obtained at relatively low cutoff energy and k-point sampling and correct them analytically, thus eliminating the necessity of running calculations with prohibitively large basis sets. The reason for the jagged appearance of the E-V curve is the discontinuous change in the number of plane waves used at the same cutoff energy but for different lattice constants. The finite basis set correction, when added to the total energy, allows one to perform calculation with a fixed number of basis states and to interpolate the results as if the more physical condition of a fixed energy cutoff were used.

The only parameter that has to be known in order for this correction term to be evaluated can be expressed as $d E_{tot} / d \ln E_{cut}$, where E_{tot} is the total energy of the system and E_{cut} is the cutoff energy. CASTEP can calculate this term automatically or you can input this parameter manually.

The value of the $d E_{tot} / d \ln E_{cut}$ derivative gives a good indication of the convergence of the calculation with respect to the energy cutoff and k-point sampling. When its value per atom (i.e., the value from prefix.cst divided by the number of atoms) is smaller than 0.01 eV $atom^{-1}$, the calculation can be considered very well converged. A value of 0.1 eV $atom^{-1}$ is sufficient for most calculations.

Optical properties

In general, the difference in the propagation of an electromagnetic wave through vacuum and some other material can be described by a *complex refractive index.*

Eq. 7 $$N = n + iK$$

In vacuum it is real, and equal to unity. For transparent materials it is purely real, the imaginary part being related to the *absorption coefficient* by,

Eq. 8 $$\eta = \frac{2k\omega}{c}$$

the fraction of energy lost by the wave on passing through a unit thickness of the material concerned. This is derived through considering the rate of production of Joule heat in the sample.

The *reflection coefficient* can be obtained for the simple case of normal incidence onto a plane surface by matching both the electric and magnetic fields at the surface,

Eq. 9 $$R = \left|\frac{1-N}{1+N}\right|^2 = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}$$

However, when performing calculations of optical properties it is common to evaluate the *complex dielectric constant*, and then express other properties in terms of it. The complex dielectric constant $\varepsilon(\omega)$ is given by,

Eq. 10 $$\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2$$

and hence the relation between the real and imaginary parts of the refractive index and dielectric constant is,

Eq. 11 $$\varepsilon_1 = n^2 - k^2 \varepsilon_2 = 2nk$$

A further frequent form for the expression of optical properties is the *optical conductivity*,

Eq. 12 $$\sigma = \sigma_1 + i\sigma_2 = -i\frac{\omega}{4\pi}(\varepsilon - 1)$$

But, this is most useful for metals, which are not treated in this package (while there is the facility to include DC conductivity and Drude damping).

A further property we may calculate from the complex dielectric constant it the loss function. It describes the energy lost by a point electron passing through a homogeneous dielectric material, and is given by,

Eq. 13 $$Im\left(\frac{-1}{\varepsilon(\omega)}\right)$$

Connection to experiment

Experimentally, the most accessible optical parameters are the absorption $\eta(\omega)$, and the reflection $R(\omega)$ coefficients. In principle, given the knowledge of both these, the real and imaginary parts of N can be determined, through Eq. 8 and Eq. 9. Eq. 10 allows expression in terms of the complex dielectric constant. However, in practice, the experiments are more complicated than the case of normal incidence considered above. Polarization effects must be accounted for, and the geometry can become quite involved (for example, transmission through multi-layered films or incidence at a general angle). However, this is a problem of optics, and would needlessly complicate the microscopic origin of the optical properties. We consider only normal incidence, but polarization effects are taken into account. For a more general discussion of the analysis of optical data see Palik, 1985.

Connection to electronic structure

The interaction of a photon with the electrons in the system under study is described in terms of time

dependent perturbations of the ground state electronic states. Transitions are caused between occupied and unoccupied states by the electric field of the photon (the magnetic field effect is weaker by a factor of *v/c*). When these excitations are collective they are known as plasmons (which are most easily observed by the passing of a fast electron through the system rather than a photon, in a technique known as Electron Energy Loss Spectroscopy, described by Eq. 13 -- since transverse photons do not excite longitudinal plasmons). When the transitions are independent they are as single particle excitations. The spectra resulting from these excitations can be thought of as a joint density of states between the valence and conduction bands, weighted by appropriate matrix elements (introducing selection rules).

Evaluation of the dielectric constant

We calculate the imaginary part of the dielectric constant, which is given by,

$$\varepsilon_2\left(\mathbf{q} \to \mathbf{0}_{\hat{\mathbf{u}}}, \hbar\omega\right) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{\mathbf{k},v,c} \left|\langle \psi_{\mathbf{k}}^c | \hat{\mathbf{u}}.\mathbf{r} | \psi_{\mathbf{k}}^v \rangle\right|^2 \delta\left(E_{\mathbf{k}}^c - E_{\mathbf{k}}^v - E\right)$$

Eq. 14

where **u** is the vector defining the polarization of the incident electric field.

This expression is similar to Fermi's Golden rule for time dependent perturbations, and $\varepsilon_2(\omega)$ can be thought of as detailing the real transitions between occupied and unoccupied electronic states.

Since the dielectric constant describes a causal response, the real and imaginary parts are linked by a Kramers-Kronig transform. This is used to obtain the real part, $\varepsilon_1(\omega)$.

Details of the computation

Brillouin Zone integrations

The current approach to integration over the Brillouin Zone involves taking a symmetrized Monkhorst-Pack grid, and smearing each energy level with a Gaussian spread function. Note that we do not take the approach of using a phenomenologically justified Lorentzian smear since it is found that unrealistic lifetimes have to be applied if a reasonable number of k-points are to be used.

Evaluation of Matrix Elements

The matrix elements that are required to describe the electronic transitions in Eq. 14 are $\langle \psi_{\mathbf{k}}^c | \mathbf{r} | \psi_{\mathbf{k}}^v \rangle$, which may normally be written as $(1/i\omega m)\langle \psi_{\mathbf{k}}^c | \mathbf{P} | \psi_{\mathbf{k}}^v \rangle$ allowing straight forward calculation in reciprocal space. However, this depends on the use of local potentials (Read and Needs, 1991), while in CASTEP non-local potentials are the norm. The corrected form of the matrix elements are,

$$\langle \psi_{\mathbf{k}}^c | \mathbf{r} | \psi_{\mathbf{k}}^v \rangle = \frac{1}{i\omega m}\langle \psi_{\mathbf{k}}^c | \mathbf{P} | \psi_{\mathbf{k}}^v \rangle + \frac{1}{\hbar\omega}\langle \psi_{\mathbf{k}}^c \left(\left|V_{nl}\right|, \mathbf{r}\right) \psi_{\mathbf{k}}^v \rangle$$

Eq. 15

Polarization

For materials that do not display full cubic symmetry, the optical properties will display some anisotropy. This can be included in the calculations by taking the polarization of the electromagnetic field into account. As mentioned above, the unit vector **u** defines the polarization direction of the electric field. When evaluating the dielectric constant there are three options.

Polarized

This requires a vector to define the direction of the electric field vector for the light at normal incidence to the crystal.

Unpolarized

This takes the vector supplied as the direction of propagation of incident light at normal incidence to the crystal. The electric field vector is taken as an average over the plane perpendicular to this direction.

Polycrystal

No direction need be specified, the electric field vectors are taken as a fully isotropic average.

Scissor operator

As discussed below, the relative position of the conduction to valence bands are found to be in error when the Kohn-Sham eigenvalues are used. In an attempt to "fix" this we allow a rigid shift of the conduction band. This is given the formal name of a *scissor operator*.

Limitations of the method

Local field effects

The level of approximation used here does not take any local field effects into account. These arise from the fact that the electric field experienced at a particular site in the system is screened by the polarizability of the system itself. So, the local field is different from the applied external field (i.e., the photon electric field). This can have a significant effect on the spectra calculated (see the example of bulk Silicon below), but it is prohibitively expensive to calculate for general systems at present.

Quasiparticles and the DFT bandgap

In order to calculate any spectral properties we have been forced to make the identity between the Kohn-Sham eigenvalues and the quasiparticle energies. Although there is no formal connection between the two, the similarities between the Schr錂inger-like equation for the quasiparticles and the Kohn-Sham equations allow the two to be identified. For semiconductors, it has been shown computationally (comparing GW and LDA bandstructures) that most of the difference between Kohn-Sham eigenvalues and the true excitation energies can be accounted for by a rigid shift of the conduction band upwards with respect to the valence band (Goodby et al. 1992). This is attributed to a discontinuity in the exchange-correlation potential as the system goes from (N)-electron to (N+1)-electron during the excitation process (Goodby 1992). There can, in some systems, be considerable dispersion of this shift across the Brillouin Zone, and the scissor operator we use here will be insufficient.

Excitonic effects

In connection with the absence of local field effects, excitonic effects are not treated in this formalism. This will be of particular importance for ionic crystals where such effects are well known.

Spin-polarized systems

Spectra generation for spin polarized systems is not implemented at present. This will preclude calculations of magnetic systems.

Others

The nonlocal nature of the GGA is not taken into account on evaluating the matrix elements, but it is expected that this will have a small effect on the calculated spectra. Clearly, phonons and their optical effects have been neglected. Finally, there is an intrinsic error in the matrix elements for optical transition due to the fact that pseudo-wavefunctions have been used (i.e., they deviate from

the true wavefunctions in the core region), leading to small numerical errors. However, the selection rules will not be changed.

Note that optical properties calculation is not yet available with ultrasoft pseudopotentials.

CASTEP methodology

This section gives some general guidelines concerning the most important parameters that must be considered in setting up a CASTEP run.

K-point sampling

An appropriate choice of the k-point set is important for achieving balance between accuracy and efficiency. The default spacing between Monkhorst-Pack points is 0.1 E-1 for insulators and 0.05 E-1 for metals, since metallic systems require better sampling. This normally produces sufficient sets, e.g., 2x2x2 for a conventional Si cell. You should check whether suggested odd values of Monkhorst-Pack parameters can be profitably increased by one. This substitution is done automatically for cubic and hexagonal cells, but there are other cases where the symmetrized set generated for, e.g., a 2x2x3 parameter set, contains as many points as a 2x2x4 set. It should be remembered that an increased k-point set reduces the finite basis set correction and makes cell relaxation more accurate at a fixed energy cutoff.

FFT grid dimensions

These parameters are derived automatically from the specified energy cutoff. It is recommended increase the values slightly when using gradient corrected change-correlation functionals (GGA or GGS).

In addition, there should be an extra safety margin for cell optimization runs, since the FFT grid that was sufficient for the original cell might become too small for the final one. Thus, an approximately 10% increase in grid dimensions is recommended if cell vectors are expected to change significantly during an optimization run. Furthermore, the CASTEP interface will automatically increase the recommended grid if ultrasoft potentials are used: this is required to accurately reproduce the augmentation charge.

Electronic minimizer

CASTEP provides an option of using either a density mixing scheme or the total energy minimization scheme (either band by band, BB, or all bands, AB, although band by band method is not supported if ultrasoft potentials are used).

The default method is the density mixing scheme. In this scheme the sum of electronic eigenvalues is minimized in the fixed potential instead of self-consistent minimization of the total energy. The new charge density at the end of the step is mixed with the initial density and the process is repeated until convergence. A number of options are supported for the mixing step: linear mixing, Kerker mixing, and Pulay mixing, in order of increasing robustness. It is possible to use either a conjugate-gradient based approach to minimize the sum of eigenvalues, or the residual minimization method, which uses the DIIS (direct iteration in the inverse subspace) scheme (note that only the CG-based scheme is available for ultrasoft pseudopotentials). A slightly more elaborate scheme that involves separate mixing of spin density has been developed for spin-polarized calculations.

The density mixing scheme typically offers at least a factor of 3 acceleration even on moderate size insulator systems. The main advantage of the density mixing scheme is that metallic systems can be reliably converged in a relatively small number of steps.

For both BB and AB methods, the total energy is minimized in the space of plane-wave expansion coefficients for wavefunctions using the preconditioned conjugate-gradient technique.

The BB minimizer updates one electronic band at a time, and thus performs many

orthonormalization operations to maintain all the wavefunctions normalized and orthogonal.

The AB minimizer updates all bands at once and is typically 2-3 times faster, due to savings in the orthogonalization procedure. However, memory requirements are much higher for the AB minimizer, typically at least twice that for the BB minimizer.

Real- and reciprocal- space pseudopotentials

Most pseudopotentials used by CASTEP are nonlocal. This means that, to mimic the scattering properties of an all-electron atom, we have to use a different scattering potential in each angular momentum channel. These potentials, however, are different only outside the core region of the atom, which makes real-space representation feasible.

The default choice is to use pseudopotentials in reciprocal space, that is, the $V\Psi$ operation is performed as a summation in reciprocal space. This is a natural procedure for wavefunctions that are represented by their plane-wave expansion coefficients. However, for large unit cells real-space evaluation of the $V\Psi$ term in the Hamiltonian becomes significantly faster than reciprocal-space evaluation. Indeed, the nonlocal part of the pseudopotential is nonzero only within the core region and is thus zero nearly everywhere in the large cell (the cell that is much larger than the core region of one particular atom). Thus it becomes more efficient to evaluate the $V\Psi$ product in real space and to use Fourier transformation to obtain the values in reciprocal space.

Transformation of the pseudopotentials to real space is performed by CASTEP UI as part of the input file creation procedure. The output of the transformation process is saved to prefix.cst_pstrans file. It is in general sufficient to check the magnitude of the opti parameters (listed in the textport) to be confident in the quality of transformation. An additional quality check is to examine the www error function, which should be small (less than 1e-3) for all values of wave vector q.

The use of real-space potentials increases the memory requirements for a CASTEP run, typically by 20-40%. Fine tuning of the transformation procedure can decrease this memory overhead. This requires changing the core radii in the Real Space Potentials Preferences panel to smaller values.

There is no real space option for ultrasoft pseudopotentials.

Geometry optimization

The main advantage of the new BFGS minimizer is the ability to perform cell optimizations, including optimization at fixed external stress. It is important to set up the calculation correctly in order to achieve the best performance of the minimizer.

First, if cell optimization is required, it is highly recommended to use a basis set correction term. Its calculation is not too costly (10- 30% of the self-consistent electronic minimization at the first iteration) relative to the advantages it provides. In addition, the default convergence criteria are generally reasonable and compatible, that is, they are usually satisfied approximately at the same time. It is possible to increase tolerance for the rms stress from 0.1 GPa to higher values if the bulk modulus of the substance in question is high. Indeed, this criterion should be formulated in relative units with respect to the elastic constants of the material; thus, the absolute value of 0.1 GPa chosen as the default is somewhat arbitrary.

Cell optimization runs might encounter problems if basis set correction is not used or if the energy cutoff is so low that the correction is not accurate. If this happens, an optimization run might stop with a message that the energy has converged but the stress is still nonzero. This reflects an inconsistency between energy and stress due to either absence of a correction term or incomplete correction for small cutoff energies. The minimizer attempts to find the energy minimum rather than the stress zero, since the former is more meaningful under the circumstances.

Another potential pitfall is the use of the cell minimizer when the starting geometry is very different from the final one. Finite basis set correction does depend on the cell variables, although this dependence is disregarded by the minimizer. In addition, the effective cutoff energy changes when the cell geometry is modified (it is the number of plane waves that is kept fixed). If this change takes

the E_{tot} (ln E_{cut}) function far away from the point that was used to evaluate the finite basis set correction, the results will not be accurate. You should compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two is large. The final configuration can be accessed by loading the appropriate output file for analysis in CASTEP UI.

Metallic systems

The main difference between metals and insulators from the technical point of view is that the number of occupied bands is not the same at different k-points in the Brillouin zone. The number of occupied bands for insulators is calculated as one half the total number of valence electrons, but this approach is not suitable for metals. Partial occupancies are introduced to eliminate discontinuous changes in total energy that are created when an energy band crosses a Fermi level during SCF minimization.

The overall strategy in CASTEP is as follows. The number of bands has to be slightly higher than would be required for an insulator- the default is to add four extra bands, but it might be necessary to add more bands if convergence is slow. An artificial electronic temperature is then introduced by assuming gaussian-like smearing of each energy level. Occupation numbers are deduced from the ratio of the area of the gaussian that falls below the Fermi level to its total area. Thus, a level deep in the valence band has an occupation number of 1, a level directly on the Fermi surface has an occupation number of 0.5, and a level high above the Fermi energy is empty. The smearing width is periodically halved during the CASTEP run. The latter procedure is more important for stable runs with the BB (or AB) minimizer, and in that case it is recommended to use a high initial value for smearing, about 2 eV. The density mixing scheme is much less sensitive to the smearing value, and it is sufficient to start with 0.4 eV, thus making a significant saving on the run time.

The initial and final width and the frequency of halving are controlled by options on the Metal - Preferences control panel that opens from the CASTEP SCF Options control panel when METAL is selected as the material under study.

The total energy calculated by CASTEP for metals is corrected for the fact that it now includes an artificial electronic entropy contribution. This correction is possible since there exists a closed analytical form for the dependence of the total energy on the smearing width s (or the electronic temperature). In principle, one needs to evaluate E_{tot} (s -> 0) to obtain a physically meaningful energy. In the past, values for s as low as 0.01 eV have been used to calculate the converged energy. The total energy correction described above allows you to use a much higher smearing width (up to 1 eV) and still obtain results converged with respect to s. The advantage is the added stability of the calculation, where occasional Fermi level crossings do not create instabilities. However, there is no simple expression for a similar correction for either atomic forces or stress on the unit cell.

As a result, geometry optimizations for metals should be performed with great caution. You should use smaller smearing values than for single-point energy runs. The calculated forces will be more accurate but there is a risk of instability since changes in atomic geometry are likely to cause reordering of bands and some Fermi level crossings. Cell optimization is very problematic for metal systems, since the stress tensor might be affected by nonphysical contributions from nearly empty conduction bands. The total energy is probably the most reliable quantity that can be calculated for metallic systems.

Using the CASTEP user interface

CASTEP is invoked within the Cerius² program by first selecting the Quantum 2 module from the module pullright and then selecting **CASTEP** from the deck of cards.

A typical CASTEP job involves three phases:

1. Setting up the job -- Prepare the model and specify the calculations to be performed.

2. Running and controlling the job -- Specify the machine on which you want to run the job and start the job. The input files generated by Cerius² are then passed to CASTEP for execution. Jobs can be monitored and stopped, and necessary files can be

transferred to and from remote systems using the CASTEP module's job control facilities.

3. Studying the output -- Analyze the largely numeric data output from the CASTEP run.

Setting up a CASTEP job

Setting up a CASTEP run involves generating a number of input datafiles that define the system of interest and the type of calculations that you want to perform upon that system (see "CASTEP input and output datafiles" on page 40). The CASTEP module considerably simplifies job specification and setup because it generates the appropriate input files for you.

You can load, edit, and refine the model on which to perform calculations using any of the Cerius² Visualizer tools and applications. The options that define the type of calculations you want CASTEP to perform on that model (such as the task, approximation method, and basis set to use) are accessed through buttons, popups, dialog boxes, and so on, that appear logically grouped by function on the CASTEP module's control panels. From the current model and the settings of these controls, the CASTEP module generates the input datafiles necessary to define both the system and the calculations you want to perform.

For a full description of the procedures and controls necessary for setting up a CASTEP job, see "Setting up and running a CASTEP job" on page 41.

Running and controlling a CASTEP job

When you are satisfied that your model and calculation options are correctly defined, you are ready to run your job. At this point, the CASTEP module generates and saves the input datafiles (with a user-defined file prefix) and passes them to the CASTEP application to be run. You can also restart a previous run that was stopped for some reason (provided required datafiles are still present) or start a run by passing previously saved input files to CASTEP.

CASTEP can be run interactively or in background or via the Network Queueing System (NQS), if installed, on the local system or a remote host. Multiple jobs can be initiated on the same or different systems; background and NQS jobs can proceed independently of the Cerius² session in which they were initiated. For more information about processing modes, see "Setting up and running a CASTEP job" on page 41.

For a full description of the procedures and controls needed to run a CASTEP job, see "QMW job execution and control".

Job control

CASTEP jobs started in background or via NQS can run for as long as several days and, when complete, terminate silently. The CASTEP module provides job control facilities that enable you to readily monitor job progress and transfer necessary datafiles to and from remote systems. For a description of the CASTEP module's job control facilities, see "Controlling CASTEP jobs" on page 56.

Studying CASTEP output

If CASTEP terminates successfully, the results of the run are written to output files with the same prefix as the input file (see "CASTEP input and output datafiles" on page 40). The CASTEP module's analysis tools allow you to obtain more readily usable information from the complex data in these files. For example, you can plot band structures and the density of electronic states, calculate and display a charge density isosurface or slice, and generate trajectory files from dynamics output. For further information about details of the CASTEP module's analysis tools, see "Studying CASTEP output" on page 58.

CASTEP input and output datafiles

Communication between CASTEP and the CASTEP user interface occurs via several input and output datafiles. These files share a common, user-defined prefix for any particular CASTEP run, as outlined in the table below:

Datafile name	Purpose
Input files:	
run_name.rundat	Runtime parameters.
run_name.param	Parameters required for array dimensions.
run_name.geom	Structural description of your molecular system in CASTEP format.
run_name.recpot	Reciprocal-space potential.
run_name.realpot	Real-space potential (if Real Space option is used).
run_name.symm	Symmetry information (if symmetry is higher than P_1).
run_name.ewdata	Automatically generated fixed file (same for all).
run_name.optim	Constraints for geometry optimization and initial Hessian matrix (only created when the **BFGS** option is selected on the Geometry Optimization control panel).
Output files:	
run_name.gm*	Structure/electron band information (binary data).
run_name.charge*	Charge density information (binary data).
run_name.wavfun*	Wavefunctions (binary data).
run_name.occnum*	Band occupation numbers (for metals).
run_name.bands	Electron bands (if computed).
run_name.coord	Coordinates from molecular dynamics or geometry optimization run.
run_name.veloc	Velocities from molecular dynamics run.
run_name.temper	Temperature from molecular dynamics run.
run_name.hamilt	Constant of motion from molecular dynamics run.
run_name.cst	CASTEP logfile.
run_name.optim_out	Like *run_name*. optim, but with the final Hessian matrix.
run_name.cell	Cell constants and stress tensor.
run_name.force	Forces from molecular dynamics or geometry optimization run.
* Output datafiles required to restart a CASTEP job. All the usual input files that define the job are also required. For details see "Restarting a previous run" on page 53.	

Setting up and running a CASTEP job

In using the CASTEP module, setting up and running a CASTEP job is a relatively straightforward matter, performed primarily from the Run CASTEP control panel. To reduce the procedure to its simplest terms, all you need to do is prepare the molecular system you want to study, set the CASTEP options that define the nature of the calculations to be performed, and identify the machine on which the job is to be run.

To run the most basic single-point energy calculation using the default method, basis set, and other options on your local machine, you need only prepare your model and click RUN. The CASTEP module uses settings suitable to your chosen options to create an appropriate input file and passes that file to the CASTEP application for execution. To perform more complex calculations using different methods, basis sets, and so on, you simply go to other easily accessible control panels from which the appropriate options are available.

Preparing the molecular system for study

Periodic systems

For periodic systems, you need only load or sketch and build (using the **CRYSTAL BUILDER** card under **BUILDERS 1**) your model in the current model space.

Nonperiodic systems

If you want to study nonperiodic systems (including defects, surfaces, and molecules), you need to use supercell approximation techniques. To do this, simply construct a large unit cell containing the molecular configuration in question and repeat it periodically throughout space. By studying the properties of the system for larger and larger unit cells, you can gauge the importance of the induced periodicity and then systematically filter out that periodicity.

Defining tasks, approximation methods, and basis sets

The most fundamental parameters that define the characteristics for a CASTEP run are the task (that is, the primary objective of the calculation), and the approximation method and basis set to be used to perform that task. Basic choices for these fundamental factors can be made from popups on the Run CASTEP control panel, with further choices and related options available on other control panels accessible from the Run CASTEP control panel.

Task

The task defines the type and primary objective of the calculations that CASTEP is to perform for your structure. A wide variety of tasks are available, and some may be combined. The objective of some typical tasks are:

- Single-point energy calculation.
- Geometry optimization.
- Molecular dynamics.

No additional options are available for single-point energy calculations. Related options for optimization or dynamics can be accessed by clicking the **More...** button beside the **Tasks** popup on the Run CASTEP control panel.

Method

The following can be used to describe exchange-correlation interactions within density functional theory. These are:

- **LDA** -- Local density approximation (Perdew-Zunger parametrization).
- **GGA** -- Gradient-corrected LDA (Perdew-Wang 1991, generalized gradient approximation).

- **LSDA** -- Local Spin Density Approximation (Perdew-Zunger parametrization).
- **GGS** -- Gradient-corrected LSDA (Perdew-Wang 1991).

Basis set

Bloch's theorem states that the electronic wavefunctions at each k point can be expanded in terms of a discrete plane-wave basis set. In principle, an infinite plane-wave basis set is required to expand the electronic wavefunctions. However, coefficients for plane waves with small kinetic energy are typically more important than those with large kinetic energy. Consequently, plane-wave basis sets can be truncated to include only plane waves that have kinetic energies less than some specified cutoff energy.

You can choose from three settings for plane-wave expansion of wavefunctions using the Basis Set popup. These settings are **COARSE**, **MEDIUM**, **FINE** and **PRECISE**.

Specific energy cutoff values defined by these settings depend on the convergence properties of the pseudopotentials used for the current model. Each pseudopotential file provided with CASTEP contains three suggested cutoff energies that correspond to the **COARSE**, **MEDIUM** and **FINE** settings (**PRECISE** is defined as 1.1*FINE). These values were determined from convergence tests for single atoms and diatomic molecules, and they roughly correspond to the total energy convergence of 2, 0.3 and 0.1 eV/atom, respectively.

When using ultrasoft potentials, it is generally unwise to reduce the plane-wave energy cutoff below the **COARSE** values set by the software. This may lead to an inadequate representation of the augmentation charge. In some cases, this may manifest itself as a negative charge density in real space and may lead to inaccuracies in, for example, geometry optimization. In particular, low energy cutoff values might cause inaccurate representation of the augmentation charge, which will be reflected in non-monotonic behavior of the total energy as a function of the cutoff energy. It has been observed that some potentials might give lower total energy for small values of cutoff energy than the converged value at the **FINE** level of accuracy, in particular in the molecular systems. However, all the potentials have been tested at a **FINE** or **PRECISE** level of accuracy on at least two solid state examples: all the test cases give cell parameters within 2% of the experimental data, and in most examples the accuracy is in fact within 1%. In other words, **COARSE** is not a safe choice, and it should be avoided except for very rough calculations.

You can also specify any appropriate value for the plane-wave basis set energy cutoff and specify fast Fourier transform (FFT) grid dimensions from the CASTEP Basis Set control panel, which is accessed by clicking the **More...** button next to the **Basis Set** popup on the Run CASTEP control panel. Changing the cutoff energy causes recalculation of the FFT grid. It is not recommended to make the FFT grid dimensions smaller than the ones suggested by the interface.

Other calculation options

Numerous other parameters and options that affect the calculations made during your CASTEP run can be set using the CASTEP module. The controls for these options are grouped by function and located on other control panels accessible from the Run CASTEP control panel.

Pseudopotentials

Pseudopotentials for each element are initially loaded from potential files provided. Potential files have file prefixes that relate to the chemical symbol of the corresponding element, for example, Ag_00.usp or Ag_00.recpot for silver. The different file suffixes refer to the different types of pseudopotential (see the *CASTEP theory* section). CASTEP combines all the necessary pseudopotentials into a single .recpot file before starting a job. Note that for real-space representation of the nonlocal component of pseudopotentials, an additional combined potential file with a .realpot extension isrequired, and is also generated by CASTEP before starting the job.

The default pseudopotentials are ultrasoft (.usp extension). They require a quite low energy cutoff and guarantee good transferability, that is, the same potential correctly reproduces the valence electron scattering by the ionic core in different chemical environments. The second best choice is

the .recpot potentials, the standard norm-conserving pseudopotentials in the separable KleinmanBylander form. Norm-conserving potentials for the first-row elements (C, O, N, etc.) and for transition metals are optimized to achieve the best possible convergence with respect to the number of plane waves in the basis set.

The pseudopotential concept allows only valence electrons to be considered in calculations, simplifying them enormously. However, the downside of this approach is that such potentials become nonlocal (that is, they depend on angular momentum). For a large system, computation of the action of such potentials on the wavefunction can become a significant performance bottleneck. This can be overcome by using nonlocal potentials in real, rather than reciprocal, space. The CASTEP module incorporates code to handle the transformation of standard reciprocal-space potential files into real space.

You can view the potentials being used for the elements in your model, load custom potentials from a file, and choose between reciprocal- and real-space representations for the nonlocal component of pseudopotentials from the CASTEP Potentials control panel, which is accessible by clicking the **Pseudopotentials...** button on the Run CASTEP control panel.

Electronic minimizer

The settings for the electronic minimization scheme can be found on the CASTEP SCF Options panel. The default scheme is the density mixing one with the conjugate gradient (CG) method for eigenvalues minimization. Note that when using the density mixing method, the SCF energy no longer decreases monotonically to the final converged SCF energy, and unconverged energies may have values lower than the final converged energy. This behavior is due to the fact that in the density-mixing method, the Harris functional for the energy is used rather than the Kohn-Sham functional. Unlike the Kohn-Sham functional, the Harris functional does not necessarily have a minimum at the SCF solution.

The density-mixing scheme is controlled by a number of additional parameters that can be set using the CASTEP Density Mixing Options panel, which is accessible from the CASTEP SCF Options panel. These correspond to the final six entries in the .rundat file. Most of the additional parameters determine how the input density for the next iteration is calculated from the previous input and output density (or densities). The default values for these parameters should be adequate for most systems. For some complex systems (including some spin-polarized systems) or systems containing certain "difficult" atom types, it may be necessary to modify (usually reduce) the density mixing amplitude somewhat. It is unlikely that the other parameters will need to be changed from their default values.

In addition to the parameters which define how the density is mixed, there is also a choice of algorithms to use in optimizing the wavefunctions. By default a conjugate-gradients (CG) algorithm is used. This is the more robust algorithm. The RMM-DIIS method may also be selected. This may result in an acceleration (of roughly 30%) in many cases, as it requires fewer wavefunction orthogonalizations. However, caution is advised in the use of the RMM-DIIS method since it is not guaranteed to converge to the lowest set of eigenvalues.

This is a particular problem for insulators. For this reason, when the RMM-DIIS method is selected, a number of conjugate-gradients iterations are carried out before switching to RMM-DIIS. This number (3 by default) is controlled by the RM_DELAY parameter in the .rundat file. Generally we recommend use of the CG algorithm, especially for insulators. However you may wish to experiment with the use of the RMM-DIIS method. Note that the RMM-DIIS method is, as yet, not available for use with ultrasoft pseudopotentials.

For norm-conserving potentials, the density-mixing electronic minimization method is provided in addition to the previously available band-by-band and all-bands methods. For systems containing ultrasoft potentials there are certain restrictions on the choice of electronic minimization methods. The band-by-band method is not available since it is incompatible with the charge augmentation required by the ultrasoft potentials. In addition, the all-bands method is only implemented for insulators. The density-mixing method is available for both metallic and insulating systems. These restrictions should not be a problem, since density-mixing is the preferred method.

K-points

Using a periodic supercell, CASTEP considers electronic states only in the first Brillouin zone (Chadi et al. 1973; Joannopoulos and Cohen 1973; Monkhorst and Pack 1976; Evarestov and Smirnov 1983). Calculation of the total energy and charge density using density functional theory requires several integrals in reciprocal space (over the Brillouin zone). CASTEP approximates these integrals by numerical summation over a finite number of k points.

CASTEP uses a special k-point approach to select an optimal set of points such that the greatest possible accuracy is achieved from the number of points used. The primary method of special-point generation implemented in the CASTEP module is the Monkhorst-Pack scheme, which produces a uniform mesh of k points in reciprocal space. The quality of this representation can be verified by increasing the density of k points used in the mesh. Nonmetallic systems typically require an order of magnitude fewer points than metallic systems because, for nonmetals, electronic properties vary much more slowly in the Brillouin zone. K-point coordinates can also be calculated for band-structure plotting, using the direction scheme or can be specified manually.

Controls governing the specification of k points are found on the CASTEP k-points control panel, which is accessed by clicking the **K-Points...** button on the Run CASTEP control panel.

For many elements, more than one potential is provided. In these cases, you can inspect the textual comments in the files to establish their recommended usage in applications.

Output and SCF options

Output options

CASTEP output options governing output style, iteration backup and output, timing data, and stress tensor calculation can all be set on the CASTEP Output control panel, which is accessed by clicking the **Output Options...** button on the Run CASTEP control panel.

SCF options

Parameters governing the CASTEP self-consistent field (SCF) use during electronic structure calculations can be set from the CASTEP SCF Options control panel, which is accessed by clicking the **SCF Options...** button on the Run CASTEP control panel.

Note

It is necessary to use the SCF options panel to specify whether the material is expected to be a metal or insulator.

Optical Properties

Producing optical spectra

The calculation of optical properties involves:

- Performing a single point energy calculation to evaluate the self-consistent charge density. This allows the construction of the fixed Hamiltonian.
- For the fixed Hamiltonian, find the Kohn-Sham eigenvalues for many more k-points (for the Brillouin zone integration) and many more unoccupied states. The matrix elements for transitions between the occupied and unoccupied states are evaluated at this stage.
- From Eq. 14, $\varepsilon(\omega)$ is evaluated, for a given smearing (to assist the integration), scissor operator (to correct the bandgap error) and polarization.

- Using the above dielectric constant the optical properties required can be output.

Effects of varying the parameters

Number of Bands

It is clear from Figure 1 that $\varepsilon_2(\omega)$ converges rapidly with the number of conduction bands included. The default in the case displayed is for 12 bands in total, which corresponds to the 4+8 bands curve in Figure 1. The contributions from successive bands vary discontinuously due to selection rules. (**Number of Bands** is set on the CASTEP Optical Spectra control panel.)

Figure 1

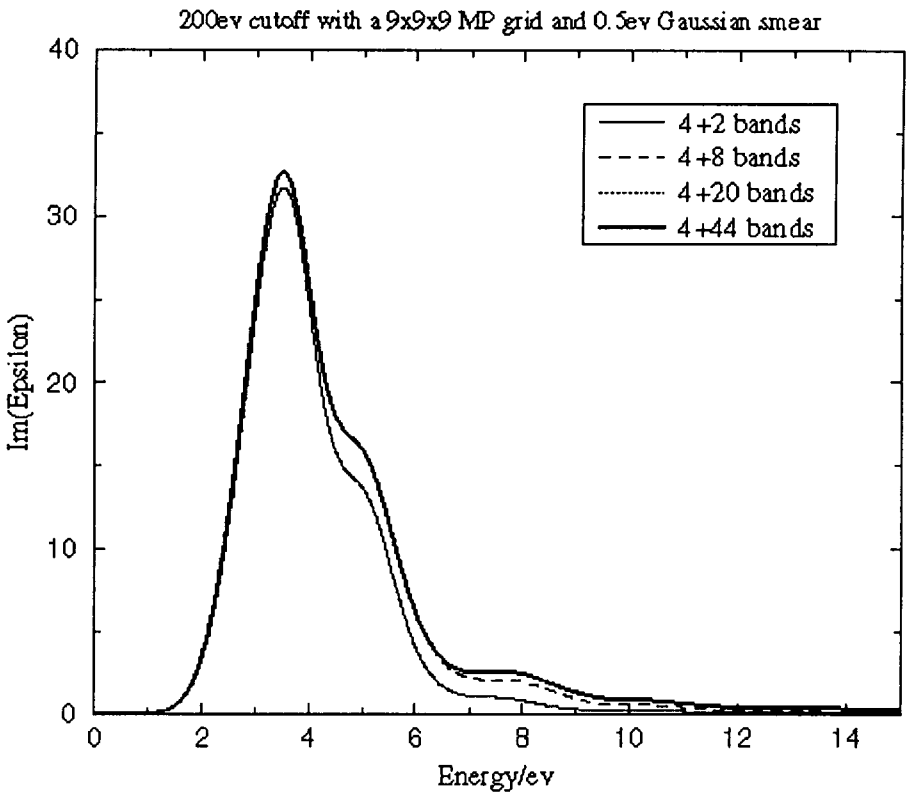


Figure 1. Silicon atom unit cell.
Convergence with number of conduction bands included.

Energy cutoff

The value of the energy cutoff that was used in the original SCF calculation of the ground state electron density is an important factor that determines the accuracy of the calculated optical properties. A bigger basis set provides more accurate self-consistent charge density and more variational freedom when searching for wavefunctions of unoccupied states. Figure 2 shows that while it is important to converge with planewave cutoff to obtain the correct energies for the spectral features, the form of those features are qualitatively rapidly reached.

Figure 2

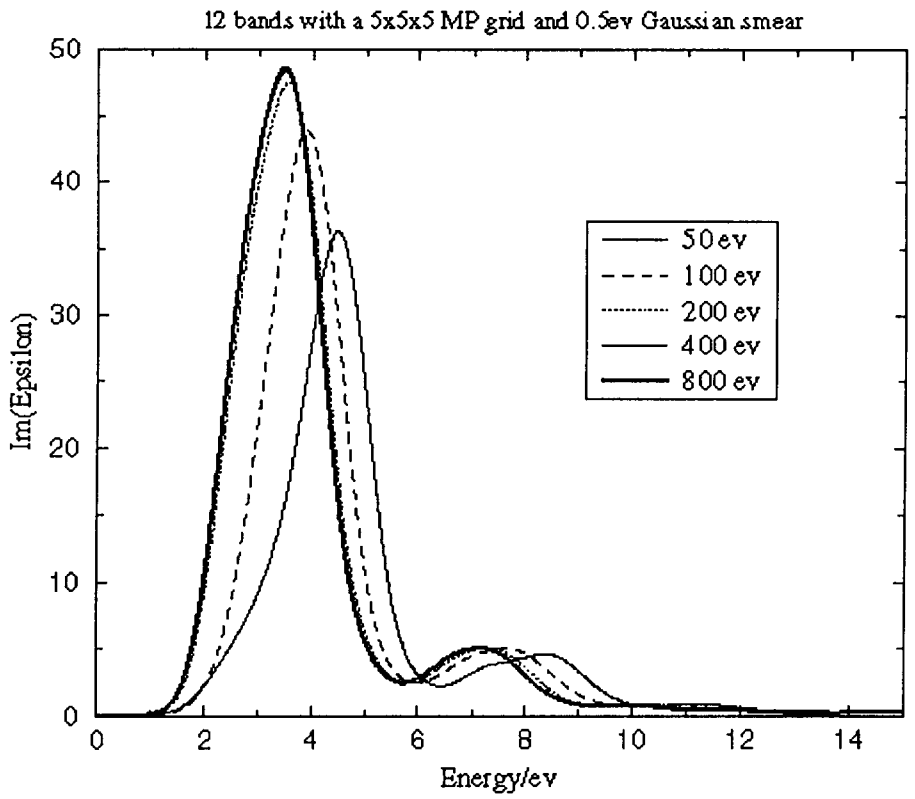


Figure 2. Silicon 2 atom unit cell.

Convergence with planewave cutoff.

Number of k-points for SCF run

The accuracy of the ground state electron density depends on the number of k-points used in the SCF run as well as on the basis set quality. Figure 3 reveals that the optical properties converge rapidly with the number of k-points used in the SCF run, which implies an insensitivity to the charge density thus calculated.

Figure 3

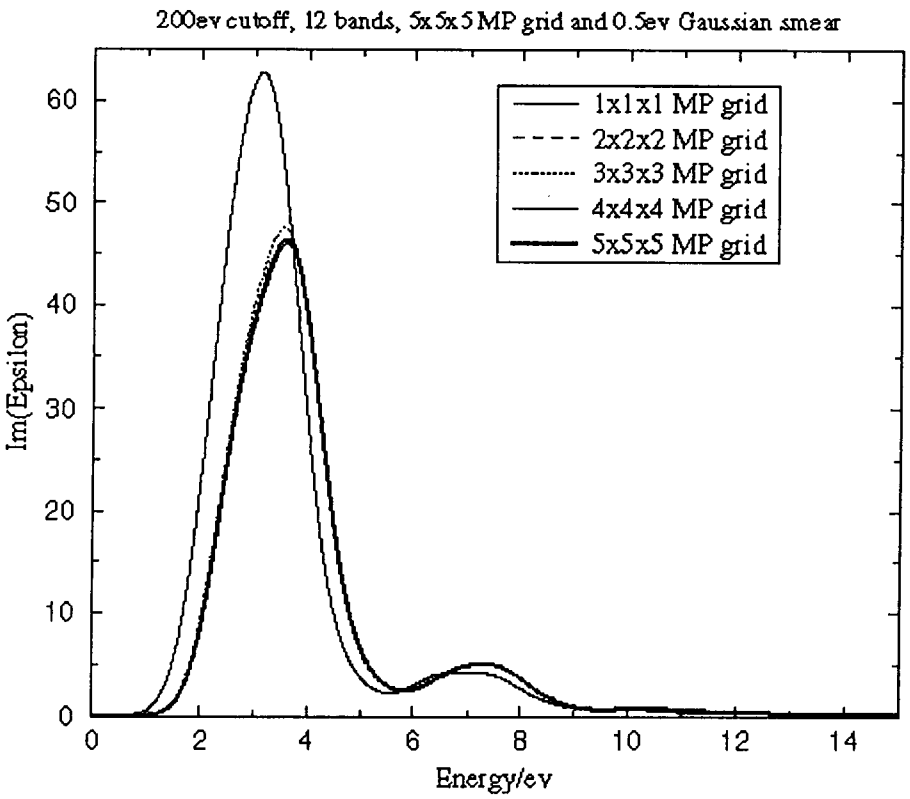


Figure 3. Silicon 2 atom unit cell.

Convergence with number of K-points for self-consistent run.

Number of k-points for Brillouin Zone integration

It is important to use a sufficient number of k-points in the Brillouin zone when running optical matrix element calculations. The matrix element changes more rapidly within the Brillouin zone than electronic energies themselves, so one requires more k-points to integrate this property accurately than is needed for an ordinary SCF run. The number of k-points can be increased by requesting smaller spacing between the k-points (specified on the CASTEP K-Points for Optics panel). Figure 4 clearly demonstrates the importance of converging the BZ integration for the optical properties with k-point density. Both energies and spectral features are strongly effected by the accuracy of this integration.

Figure 4

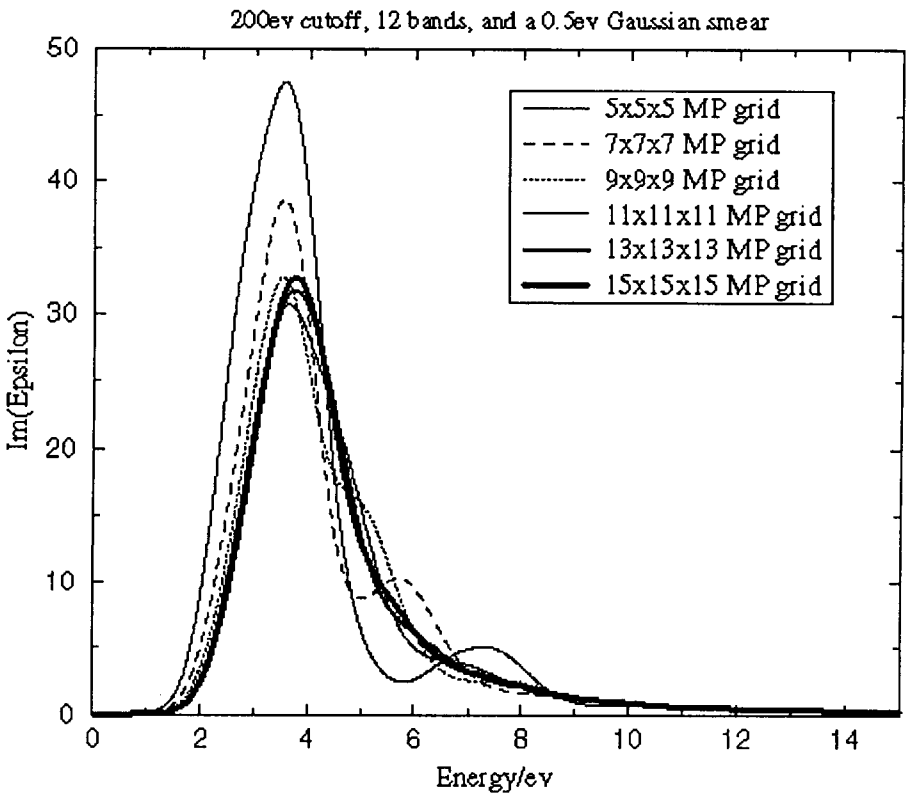


Figure 4 Silicon 2 atom unit cell.

Convergence with number of K-points in BZ integration.

The question of accuracy and precision

The effect of the various parameters on the degree of convergence achieved in the calculation of the optical properties has been described. It must, however, be kept in mind that full convergence (which will frequently lead to a highly strenuous calculation) will not always be appropriate. Experimental data is always only accurate to within some error, and the theory itself (see "Limitations of the method") is limited in accuracy.

The choice of properties to be output

All the optical properties that concern us can be expressed in terms of either the complex dielectric constant, or complex refractive index.

By default, the absorption $\eta(\omega)$ and reflection $R(\omega)$ coefficients are output on calculation of the dielectric constant. Following this, the calculation need not be repeated (for fixed scissors operator, smearing and geometry), and the optical properties may be graphed.

Geometry constraints

Geometry constraints allow you to specify which atoms and unit-cell parameters are fixed and which are allowed to move during CASTEP minimization calculations. Controls on the Atom Constraints and Cell Constraints control panels (accessed by clicking **Geometry** on the **CASTEP** menu card and choosing **Atom Constraints** or **Cell Constraints** from the pullright that appears) allow you to specify constraints for your model.

Atom constraints

A set of controls allows you to fix atomic position or allow atomic motion for all or selected atoms in the structure. This panel also allows you to color atoms according to their movability which provides a quick visual check of the correctness of the setup for atom constraints.

Cell constraints

A set of check boxes allows you to constrain or vary each of the unit cell lengths (a, b, and c) and angles (α, β, and γ). Additionally, a set of fields allows you to specify external stress to the cartesian axes x, y and z.

Cell optimization requires an overall accurate calculation, since otherwise there would be an inconsistency between stress and energy which will prevent the minimizer from finding a state with the specified external stress and a minimum energy. It is *strongly* recommended that you switch on the basis set correction (see the help text for the CASTEP Basis Set control panel) when performing cell optimization (this is a default setting for CASTEP). Even then, it is possible for the CASTEP job to terminate with a message warning about the inconsistency between stress and energy. If this happens, load the final structure of the run for analysis, set a new run with all the same parameters (basis set, K-points, etc.), and submit a new job.

Running the job

When you have defined your model and specified the task, method, basis set, and other options that determine the nature of the calculation, you are ready to run your CASTEP job. However, before you go ahead, you may want to set a few options governing the run itself.

Datafile title entry

Before you run your job, you can use the **Title** entry box to enter title information to be included in CASTEP input and output datafiles.

Input/output file naming

CASTEP input and output datafiles generated by Cerius^2 have several different file extensions. You can specify the prefix for the input files and the output files in the **File Prefix** entry box on the Run CASTEP control panel. Alternatively, you can select a filename prefix from existing datafiles using controls on the CASTEP Input File control panel (accessed by clicking the **Files...** button next to **File Prefix**).

Restarting a previous run

Provided that certain datafiles are present, CASTEP runs that have been stopped before completion (either deliberately or due to system failure) can easily be restarted by specifying the appropriate filename prefix and setting the **Restart Previous Run** option on the CASTEP Run Options control panel before clicking the **RUN** button (or the **Run Selected CASTEP Input File** button on the CASTEP Input File control panel).

In addition to all the input datafiles that defined the original job, *prefix*.gm, *prefix*.charge, *prefix*.wavfun, and *prefix*.occnum output datafiles are required. These output files are saved periodically during the CASTEP run. From the CASTEP Output control panel (accessed by clicking the **Output Options...** button on the Run CASTEP control panel), you can specify the frequency at which the files are saved and, thus, the maximum number of iterations that can be lost.

Running in background and on remote hosts

Options governing the execution of your CASTEP job, such as the mode of operation and host machine for remote jobs, are set from the CASTEP Job Control control panel. The job can be run interactively (as a foreground task), in the background, or via the Network Queueing System, if installed, on the local or a remote host.

Other related options can be set from control panels accessible from the CASTEP Job Control control panel. If you choose to run a job remotely, you should supply the name of that host and the name of the CASTEP executable on that system. If the remote host does support an rlogin operation from your local host, you also need to specify a valid user ID and password from the CASTEP Job Control Options control panel.

Go!

When you have correctly set up the parameters of the run, simply click the **RUN** button in the Run CASTEP control panel. Alternatively, you can choose to create the necessary input datafiles and save them to disk for later execution (locally or remotely) by clicking the **Save CASTEP Input Files** button on the CASTEP Input File control panel.

To set up and run a CASTEP job

1. Load or sketch and build (using the **CRYSTAL BUILDER** card under **BUILDERS 1**, if necessary) the periodic model upon which you want to perform CASTEP calculations.

2. Open the Run CASTEP control panel by choosing **Run** from the CASTEP menu card.

3. Specify the CASTEP calculation task by selecting one from the **Task** popup. For **Geometry Optimization** or **Dynamics** tasks, related options are available on control panels accessible by clicking the **More...** button beside the **Task** popup

4. Specify the CASTEP approximation method for density functional theory exchange-correlation interactions by selecting one from the **Method** popup.

5. Specify the plane-wave basis set energy cutoff by selecting one from the **Basis Set** popup. Alternatively, to fine tune this value and associated parameters:

    a. Open the CASTEP Basis Set control panel by clicking the **More...** button beside the **Basis Set** popup.

    b. Specify appropriate values for the **Kinetic Energy Cutoff** and **FFT Grid** dimensions.

6. If the default pseudopotentials and related options are not satisfactory:

    a. Open the CASTEP Basis Set control panel by clicking the **Pseudopotentials...** button.

    b. Examine the potentials for your model system and, if necessary, load custom potential files or reset the CASTEP default set of potentials.

7. If the default set of k points is not adequate, set up special k points for the job:

    a. Open the CASTEP k-points control panel by clicking the K-**Points...** button.

    b. Use the controls on the panel to generate special points, specify points manually, or set other options appropriately.

8. If the default output options (governing output style, iteration backup and output, timing data, and stress tensor calculation) are not satisfactory, respecify them:

    a. Open the CASTEP Output control panel by clicking the **Output Options...** button.

    b. Use the controls on the panel to set the output options appropriately.

9. If the default SCF options (parameters relevant for the electronic structure calculations) are not satisfactory, respecify them:

   a. Open the CASTEP SCF Options control panel by clicking the **SCF options...** button.

   b. Use the controls on the panel to set the SCF options appropriately.

10. Use the **Title** entry box to review (and, if necessary, edit) the title/comment information that will be placed in generated input datafiles and the logfile.

11. To specify run type, host, and other options governing the execution of the CASTEP job:

   a. Open the CASTEP Job Control control panel by choosing Job Control from the CASTEP menu card.

   b. Use the controls on the CASTEP Job Control control panel to set up the job appropriately.

12. Specify the datafile prefix using the **File** prefix entry box (or select one from existing files using the CASTEP Input File control panel). Next, either save the file for later execution or click the **RUN** button to start the job.

13. If you are going to submit a CASTEP job to a machine with a limited amount of memory:

   a. Open the CASTEP Run Options control panel by clicking the **Options...** button.

   b. Enter the amount of memory available in **Memory (Mb)**. CASTEP will perform a check before submitting the job and will cancel submission if the amount of memory available is insufficient.

   c. You can decrease memory requirements of CASTEP by switching off the **Keep Wavefunctions in Memory** checkbox.

14. If you are going to submit a CASTEP job to a machine with multiple CPUs, you might want to check the current setting for the number of processors:

   a. Open the CASTEP Run Options control panel by clicking the **Options...** button.

   b. If the **Processors** field is empty, CASTEP will use all the CPUs. You have to enter a number in this field if you want to use fewer CPUs.

15. If you manually changed the FFT grid, the Monkhorst-Pack mesh, the K-points, or the coordinates of the K-points themselves, switch off the **Calculate Before Running a Job** control on the CASTEP Run Options control panel.

Note

> For an exhaustive explanation of each control panel, command, popup, toggle, radio button, etc. in the GUI, please see the online help. In Cerius^2, place your cursor over a given control and press the right mouse button. A window will appear in the middle of your screen containing help text for that control. For more information on the help text system and using it, see the *Cerius^2 Modeling Environment* manual.

Controlling CASTEP jobs

CASTEP jobs can run on local or remote systems for long periods of time. Those initiated in background mode or NQS then terminate silently when they complete (although you can request that NQS jobs send you email when the job completes). These and other issues introduced in Chapter 2 (see "Quantum 2 job execution and control" on page 10) would make keeping track of your jobs extremely difficult without the job-control tools provided by the CASTEP module. Located on (or accessible from) the CASTEP Job Control control panel, these tools enable you to readily specify how and where your CASTEP jobs should run, monitor their progress, and transfer input and output datafiles to and from remote systems.

Specifying run mode and host

CASTEP jobs can be run interactively, in the background, or via the Network Queueing System (NQS), if installed, on the local system or a remote host. These choices and related options are easily set from the CASTEP Job Control control panel and the CASTEP Job Control Options control panel.

Monitoring jobs

The **Cerius2 Castep Job Status** list in the CASTEP Job Control control panel provides a summary of the status of all your recent jobs running on the local machine or remote hosts, including those queued, just started, in progress, or already complete. If necessary, you can terminate a job by selecting it from the list and clicking the **Kill Remote Job** button. If the necessary output datafiles are preserved, a killed job can be restarted later (although it will restart not from the latest iteration, but from the last saved one). You can request soft termination by clicking the **Shutdown Remote Job** button. In this case, CASTEP will complete one more SCF step, save the files and terminate.

To obtain a more accurate picture of the progress of a job, you can review the job logfile in real time via an xterm window on your graphics terminal. This window is opened automatically for all interactive jobs. You can also open this window for a background or NQS mode job by selecting that job from the **Cerius2 Castep Job Status** list and clicking the **Monitor Remote Logfile** button.

Note

Remote hosts on which a CASTEP job is running must be authorized to make connections to your X-server in order for you to monitor the logfile output from jobs in this manner. To authorize such access, type the following from a shell on your local system:

```
>       xhost remote_host_name
```

Datafile transfer

The CASTEP module automatically handles the transfer of generated input datafiles to another host when you start interactive, background, or NQS mode remote jobs. After job completion, all the output datafiles are automatically recovered for interactive mode jobs. For background mode and NQS jobs, all or selected output datafiles (as determined by settings on the CASTEP File Options control panel) can be recovered manually from the remote host by selecting that job from the **Cerius2 Castep Job Status** list and clicking the **TRANSFER files from selected job** button.

Note

The remote file system may actually be the same as your local file system (if for example it is NFS-mounted the same way on both systems. In this case, no transfer of datafiles is necessary.

Studying CASTEP output

Results from a CASTEP run are written in readable ASCII format in the job logfile (*.cst). Binary format data is output in output datafiles. For more information about these files, see "CASTEP input and output datafiles" on page 40.

You may be able to obtain manually and/or extrapolate all the information that you require from the data in the output datafiles. However, the CASTEP module provides a set of analysis tools that you can use to analyze information from these files and readily visualize the results using the Cerius² graphical display functionality. Information that can be analyzed using the CASTEP analysis tools includes:

- Model structure -- Recover and analyze geometry and trajectory.
- Band structure -- Calculate or load band structures. The results can then be plotted.
- Density of states -- Perform DOS calculations using smearing of bands. The results can then be plotted.
- Optical properties -- Calculate optical matrix elements and generate optical spectra (complex dielectric function, complex refractive index, adsorption, reflectivity, etc.)
- Charge density -- Obtain and visualize the total charge density and compare it to the superposition of densities for subsystems. Results can be displayed as a 3D surface map or a color-contoured plane slice.
- Orbitals -- Obtain and visualize the charge density that corresponds to wavefunctions in a chosen energy interval. This corresponds to orbitals displayed for molecular systems.
- Electrostatic potential -- Obtain and visualize the electrostatic potential. Results can be displayed as a 3D surface map or a color-contoured plane slice.

Accessing the tools

The CASTEP analysis tools are all accessed via the **Analyze** pullright on the CASTEP menu card. An overview of the tools follows (please see the help text for a more complete description of each option).

Files Provides access to the CASTEP File Analysis control panel, from which you can select the logfile (*.cst) from the CASTEP job to be studied.

Band Structure Provides access to the CASTEP Band Structure control panel, from which you can calculate or load band structures and plot the results.

Density of States Provides access to the CASTEP Density of States control panel, from which you can perform DOS calculations and then plot the results using smearing of bands.

Optical Spectra Provides access to the CASTEP Optical Spectra control panel, from which you can set up an additional non-self-consistent CASTEP run to generate conduction and valence band electronic energies, calculate optical matrix elements and generate optical properties in a graphical representation.

Density Provides access to the CASTEP Charge Density control panel, from which you can obtain and visualize the total charge density (obtained from the .charge output datafile) and compare it with the superposition of densities for subsystems. Results can be displayed as 3D surface maps or as 2D slices (see the Surfaces and Slices menu entries below).

Potential Provides access to the CASTEP Potential control panel, from which you can calculate and visualize the electrostatic potential. Results can be displayed as 3D surface maps or as 2D slices (see the Surfaces and Slices menu entries below).

Orbitals Provides access to the CASTEP Orbitals control panel, from which you can calculate and visualize charge density distribution for selected wavefunctions (orbitals). Results can be displayed as 3D surface maps or as 2D slices (see the Surfaces and Slices menu entries below).

Surfaces Provides access to the CASTEP Surfaces and Surfacing File control panels, from which you can display charge density, charge difference orbitals, and potential data as a three-dimensional surface.

Property Maps Provides access to the CASTEP Surface Properties control panel from which you can display charge density, charge difference, and potential data as a color-coded map on a three-dimensional surface.

Slices Provides access to the CASTEP Slices control panel, from which you can display charge density, charge difference, and potential data as 2D color-contoured plane slices.

To retrieve and analyze model data

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

The necessary data are obtained from the CASTEP run, and the model is displayed in the model window.

2. For molecular dynamics or geometry optimization runs, click the **Create trajectory file** button to generate a trajectory file from all the structures contained in the CASTEP output. this file can be further loaded into Analysis module of Cerius^2.

To analyze band structure

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

2. Open the CASTEP Band Structure control panel by choosing **Band Structure** from the **Analyze** pullright.

3. To calculate new band energies using any k-point set:

   a. Open the CASTEP k-points control panel by clicking the **Setup k-points...** button and specify the required k points. It is helpful to visualize selected paths in the reciprocal space. This can be achieved by opening the Brillouin Zone Display panel either by clicking the **Brillouin Zone Display...** button or by choosing **Brillouin Zone** from the **Geometry** pullright. Use the controls on this panel to display the Brillouin zone, high symmetry points, the currently selected path for band structure calculation, etc.

   b. From the CASTEP Band Structure control panel, specify the tolerance for calculating the band energies and the number of CG steps and bands for the calculation. The default number of bands will produce only valence (occupied) states in case of a nonmetallic system, so the number should be increased in order to study the conduction band as well.

   c. Click the **Calculate Band Structure** button. This will start another CASTEP job

(non-self-consistent) and the CASTEP Job Control control panel can be used to specify the host, etc.

4. Select the appropriate .bands output datafile (from a previous run or newly generated), using the entry box next to the **Plot from** button, then click the **Plot from** button to plot the band structure data.

5. You can switch on **Display Density of States** control, in which case the **Plot from** button will generate the plot of density of states side by side with the band structure plot.

To analyze electronic density of states

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

2. Open the CASTEP Density of States control panel by choosing **Density of States** from the **Analyze** pullright.

3. Specify the tolerance for calculating the band energies and the number of CG steps and bands for the calculation. The default number of bands will produce only valence (occupied) states, so the number should be increased to study the conduction band as well.

4. Click the **Calculate Band Energies** button. This will start another (non-self-consistent) CASTEP job and the CASTEP Job Control panel can be used to specify the host, etc. The aim of this job is to generate electronic energies on a finer Monkhorst-Pack mesh that was used for the SCF calculation. Click **Setup K-Points...** if you wish to change the default settings for the K-points.

5. Click **Display** to create a graph of density of states as a function of energy. In the case of spin-polarized calculations, you can choose whether to plot the total density of states or its components for spin-up and spin-down electrons.

6. You can skip steps 3 and 4 if you consider the number of K-points of the original SCF run sufficient, or if you are only interested in a rough estimate of the density of states.

To analyze charge density

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

2. Open the CASTEP Charge Density control panel by choosing **Density** from the **Analyze** pullright.

3. To compare the total charge density obtained from the selected job with the superposition of densities for subsystems, use the **Calculate subsystem densities** and **Subtract subsystem densities** buttons. Charge density difference calculations involve running one or more additional CASTEP jobs.

4. To calculate and display graphical representations of the calculated total charge density or charge difference data, click the **Display charge density surface** or **Display**

charge difference surface button. Additional advanced display options are available using CASTEP surface, property map, and slice display functionality:

a. Use the controls on the CASTEP Surfaces and Surfacing File control panels (accessed by choosing **Surfaces** from the **Analyze** pullright) to generate and display a surface map of the charge volume data.

b. Use the controls in the CASTEP Surface Properties control panel (accessed by choosing **Property Maps** from the **Analyze** pullright) to generate and display a color-coded map of the CASTEP charge volume data upon some other displayed surface.

c. Use the controls on the CASTEP Slices control panel (accessed by choosing **Slices** from the **Analyze** pullright) to generate and display a plane slice of the charge volume data.

To analyze orbitals

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

2. Open the CASTEP Orbitals control panel by choosing **Orbitals** from the **Analyze** pullright. This panel will display a listbox with the table of calculated band energies.

3. Select with a mouse one or more (not necessarily adjacent) line in the list box.

4. Click the **Calculate Alpha Orbitals** button to create files with the sum of the charge densities for the currently selected orbitals and to display it in the model window. There is a choice of studying the **Alpha** (spin-up), **Beta** (spin-down), or **Total** densities for spin polarized vibrations.

5. Alternatively, instead of step 3, open the CASTEP Density of States control panel by choosing **Density of States** from the **Analyze** pullright.

   a. Click the **Display** button;

   b. Choose **Pick Orbitals from DOS Plot** on the CASTEP Orbitals panel;

   c. Use the mouse to select the energy range from the density of states plot. The lines in the orbitals listbox will be selected as you do this.

   d. Proceed to step 4.

To analyze optical spectra

1. Select the appropriate .cst file:

   a. Open the CASTEP File Analysis control panel by choosing **Files** from the **Analyze** pullright.

   b. Select the appropriate .cst file.

2. Open the CASEP Optical Spectra control panel by choosing **Optical Spectra** from the **Analyze** pullright.

3. Specify the **Tolerance for Band Energies (eV)** for the calculation of band energies, and the **Number of Electronic CG Steps** and bands for the calculation. The more bans

you include, the wider will be the energy interval over which optical spectra will be calculated. Click the **Setup K-Points** button to change the default Monkhorst-Pack settings.

4. Click the **Calculate Matrix Elements** button. This will start another CASTEP job (non-self-consistent), and the CASTEP Job Control panel can be used to specify the host, etc. The aim of this job is to generate band energies on a file mesh (similar to what is done when submitting a job for a density of states calculation) and to evaluate optical matrix elements. Note that the results of this run can be used to plot density of states from the CASTEP Density of States panel.

5. Check the settings (**More...**) for dielectric function calculation (**Scissors Operator**, polarization, **Smearing Width**, output file name) and click the **Calculate Dielectric Function** button.

6. By default, reflectivity and adsorption are displayed as a function of energy in eV.

7. On the Optical Spectra control panel, change **Frequency Units** if necessary and click **Plot Optical Properties**. You can also change the set of displayed functions by clicking on the **More...** button at the bottom of the panel. The options are: **Reflectivity**; **Adsorption**; **Real/Imaginary Dielectric Function**; **Real/Imaginary Conductivity**; **n** or **k** (real/imaginary refractive index); electron **Loss Function**, or any combination thereof. You have to click the **Plot** button to see the effect of these changes.

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