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论文题目：新材料物性的第一性原理研究

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中 文 摘 要

Freeman J. Dyson 曾说过“计算机是使我们更有条理地思考的工具”。随着当前计算机科学技术的进步，计算已经与理论和实验三足鼎立，成为我们的第三种科学手段。而具体到化学和材料科学中，基于密度泛函理论的第一性原理计算方法的飞速发展和广泛应用则尤其引人注目。正是在这种背景下，本文对一些不同维度的新型材料（从固体、固体表面、纳米管到分子、团簇）进行了第一性原理研究，研究涉及的材料物性包括几何构型、电子结构、磁学性质、晶格振动和力学响应等方面。论文强调从数值计算结果中建立物理化学模型，从而获得对所研究问题本质的理解。

第一章简要介绍了密度泛函理论的基本框架和近年来的理论发展。密度泛函理论的发展以寻找合适的交换相关能量泛函为主线。近年来，各种不同泛函形式的出现使得密度泛函理论可以提供越来越精确的计算结果。另外，密度泛函理论向动力学平均场和含时理论等方面的扩展也很活跃。这些扩展使得密度泛函理论的应用领域不断扩大。

第二章所关注的是密度泛函理论的数值计算方法。应用密度泛函理论进行具体的数值计算，首先要将解析的理论离散化。基于不同的离散方案，各种数值计算方法迅速发展。从古老的有限差分、有限元到新兴的小波分析都被用来实现密度泛函理论的数值计算。与此同时，线性标度算法的日趋成熟，使得通过密度泛函理论研究诸如生物大分子之类的体系成为可能。在本章的第二部分，我们详细介绍了一种实空间双重网格能量泛函直接最小化方法以及我们在这种方法的具体程序实现方面所作的工作。这种实空间算法兼有原子基组算法和赝势平面波方法的一些优点，可望实现高效的并行化和线性标度。

从第三章开始，我们把目光转向实际材料的物性研究。第三章研究的是一类新奇的化学材料|无机电子阴离子化合物。在这类材料中，电子本身成为简单的阴离子。这种独特的结构使得这类化合物具有重要的理论意义和广泛的应用前景。现在实验上合成了两种类型的无机电子阴离子化合物。第一种通过往沸石 ITQ-4 中掺杂碱金属铯得到，理论计算结果清楚表明碱金属在沸石通道中以离子形式存在，产生的电子离域在整个通道中。另外，我们还发现掺杂不同的碱金属表现出截然不同的物理化学性质。通过改变碱金属掺杂类型，系统可以从绝缘体、半金属转变为金属。该结果显示了通过施加空间几何限制实现纳米线电子结构调控的可能性。第二种无机电子阴离子化合物通过除去钙铝石 C12A7 中的自由氧而得到。在钙铝石晶体中有许多笼状结构，一些自由氧离子分布在这些笼子中，引起对应笼子一定程度的结构畸变。几何构型优化表明，去掉自由氧离子后畸变消失，所有的笼子互相等价。额外电子总的说来是局域在笼子中的，每个笼子的电子占据几率为 1/3。电子局域化函数分析表明在带正电荷的笼子框架和局域的额外电子之间形成离子型化学键。由此，我们认为脱氧钙铝石体系是可以用电子阴离子模型来描述的。本章的工作发表在 ***J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Eur. J.***和 ***J. Chem. Phys.***上。

第四章研究了一类重要的物理材料|Na_xCoO_2。这类材料长期以来就由于以下两个原因而倍受关注。首先，其碱金属离子的高迁移率使它成为一种优秀的电极材料。另外，它还具有反常的高热电产率。最近，人们又发现该材料的水合物在温度低于约 5K 时出现超导，这使它再次成为人们瞩目

的焦点。在该材料中，钴原子处于畸变的氧八面体晶场中，Co 的 3*d* 电子决定了体系的电子结构。我们采用 DFT+*U* 方法研究了它的几何、电子和磁性质。DFT+*U* 方法可以处理过渡金属氧化物中 *d* 电子的强关联效应。我们着重研究了实验上发现电荷有序的绝缘体基态的 x = 0.5 的情形。计算结果表明，体系的性质随原子位上库仑相互作用参数 *U* 的改变而显著变化。另外，为了考察钴氧超导体中可能存在的电声相互作用，我们还用密度泛函微扰理论计算了 $NaCoO_2$ 的点阵动力学，计算结果表现出很强的各向异性，这反应了体系的强二维特性。除了一些主要由 Na 垂直平面振动贡献的声子外，大部分声子的频率随 Na 掺杂浓度及占据位置的变化很小。这两项工作发表在 ***Phys. Rev. B*** 上。

前面两章涉及的都是体相材料。在第五章，我们研究了一些低维材料。首先，是关于小分子 SF_5CF_3 的研究，它是最近新发现的一种温室气体。我们用杂化密度泛函理论计算了其电子结构和原子振动，研究表明该分子确实有超强的红外吸收。另外，在对钯纳米粒子的扫描隧道显微镜/扫描隧道显微谱（STM/STS）实验研究中，我们的实验合作者发现无序可以显著的抑制纳米粒子体系的量子尺寸效应。在钯纳米粒子电子结构紧束缚计算基础上，我们运用简单的正统理论很好地解释了扫描隧道显微谱的实验结果。MoS_2 是一种传统的润滑剂，最近人们通过 C_{60} 催化输运反应方法制备了这种材料的自组装纳米管。但是，对其几何、电子结构和力学性质的第一性原理研究表明最初提出的(3,3) 纳米管模型是不正确的。MgB_2 是一种转变温度很高的电声相互作用超导体。尽管许多实验涉及到该材料的表面性质，大部分理论研究集中在体相。我们计算了 MgB_2(0001)表面的电子结构和带心声子频率，并预言了增强的表面超导和出人意料的 STM 图象反转现象。本章的工作发表在 ***Phys. Rev. Lett., Appl. Phys. Lett., Phys. Rev. B*** 和 ***Chem. Phys. Lett.***上.

关键词：第一性原理，密度泛函理论，材料物性，无机电子阴离子化合物，钴氧超导体，MgB_2 表面，温室气体 SF_5CF_3

Properties of Novel Materials from First Principles

Li Zhenyu

ABSTRACT

Freeman J. Dyson said “The computer is a tool for clear thinking”. Along with the rapid progress of computational science and technology, computation has paralleled theory and experiment to be an important research method. For chemistry and material science, we all see that density functional theory (DFT) based first-principles calculation has become more and more popular. In this thesis, a variety of materials with different dimensions have been studied. The concerned properties include geometric parameters, electronic structure, magnetic ordering, phonon dispersion and mechanic response. We emphasis to get an essential physical or chemical picture from calculation numbers.

In the first chapter of the thesis, DFT and its recent progress have been reviewed. Finding good approximation for exchange-correlation functional is one of the main targets in DFT. With the development of modern functionals, DFT leads to more and more accurate results. In addition, fields such as extension of DFT to the time dependent region and combination of DFT with dynamic mean field theory (DMFT) also develop fast. All these progresses lead DFT applicable to a broad range of problems.

The second chapter focuses on the numerical methods. As the first step of numerical calculations, we need to discrete the analytical formulation of DFT. Based on different discretization schemes, a variety of numerical methods are introduced into DFT, i.e. the modern wavelet method. Meanwhile, some attempts to pursue the linear scaling of computational complexity in DFT are found being successful, which makes the application of DFT to large systems such as big biological molecule become possible. At the second part of this chapter, we introduce a real space composite grid direct minimization method and present its Fortran 90/95 program realization. This method combines some advantages of local bases methods and plane waves methods, and it is easy to realize highly efficient parallelization and linear scaling within this method.

Properties of real materials from first principles are considered from chapter 3. The first topic is a kind of novel chemical material named inorganic electride, where electron itself acts as the anion. Such a unique structure makes this kind of compound not only important in theory but also valuable in applications. There are two kinds of inorganic electrides being synthesized until now. The first kind of inorganic electride is obtained by intercalating alkali metal cesium into the channel of zeolite ITQ-4. Our calculation explicitly demonstrated that the alkali metal is ionized to cation within the channel and the released electron is delocalized from the cation. Further study indicated that different alkali metal within the channel gives very different properties. From Na to Rb doping, this material varies from insulator, semi-metal, to metal. Our study thus also demonstrates the possibility of nanowire electronic structure engineering by applying some geometrical confinements. The second kind of inorganic electride is synthesized by removing the clathrated oxygen from cages of mayenite C12A7 lattice. All cages are identical in the optimized geometry. The extra electron is generally localized inside the cages with an occupation probability of 1/3 per cavity, and electron localized function (ELF) analysis indicate that ionic chemical bonds are formed between these extra electrons and the positively charged framework. So we conclude that the clathrated oxygen removed mayenite should still be considered as an inorganic electride, even if not a perfect one. The results of this chapter have been published in ***J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Eur. J.*** and ***J. Chem. Phys.***

In chapter 4, we study a kind of important physical material, Na_xCoO_2, which has been originally studied as a kind of rechargeable battery material and thermoelectric material. More recently, the discovery of the superconductivity below 5 K in its hydrated x=0.35 composition makes it receive a renewed interest. In this material, cobalt locates in a distorted oxygen octahedron. The 3*d* orbitals of cobalt determine the electronic structure of the system. We use DFT+U method, which can deal with the on-site Coulomb interaction, to study its geometrical, electronic and magnetic properties. We mainly focus on the

x=0.5 case, where a charge ordered insulating ground state is found in experiments. Our calculations indicate that the properties of the material strongly depend on the parameter *U*. To shed insights on the possible electron-phonon interaction in this new superconductor, we also study the lattice dynamics of $NaCoO_2$ using density functional perturbation method. A strong anisotropy is observed, which indicate the 2D character of this material. The frequencies of most phonon modes are not strongly affected by the Na occupancy, except some modes mainly contributed from the out-of-plane vibration of Na. These two studies have been published in ***Phys. Rev. B***.

The above two chapters concern bulk materials only. Some low-dimension materials are studied in chapter 5, including SF_5CF_3 molecule, Pd clusters, MoS_2 nanotube, and MgB_2 surface. (1) SF_5CF_3 is a newly found greenhouse gas. We use hybrid DFT to study its electronic structure and atomic vibrations. Agreeing with experiments, we find a strong infrared adsorption for SF_5CF_3. (2) The suppression of quantum confinement effect by disorder is studied via tight-binding electronic structure calculation and orthodox theory simulation of the scanning tunneling spectroscopy (STS). (3) MoS_2 is a traditional lubricant. Recently, people synthesized self-assembly MoS_2 nanotube bundles by C_{60} catalysis transport reaction. We study their electronic and mechanic properties from first principles calculations. The original (3,3) nanotube model is found to be incorrect. (4) MgB_2 is a kind of electron-phonon superconductor with relatively high Tc. We study the electronic structure and zone-center phonon frequency of MgB_2 (0001) surface. An enhanced surface superconductivity and an unexpected STM image reversal are predicted. The results of this chapter have been published in ***Phys. Rev. Lett., Appl. Phys. Lett., Phys. Rev. B*** and ***Chem. Phys. Lett.***

Keywords: first principles; density functional theory; inorganic electride; cobalt oxide superconductor; MgB_2 surface; green house gas SF_5CF_3