论文中英文摘要

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论文题目：纳米材料的理论研究及线性标度电子结构方法的发展

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中 文 摘 要

近年来相关理论和数值算法的飞速发展，使得基于密度泛函理论的第一性原理方法在凝聚态物理、量子化学和材料科学中得到非常广泛的应用。由于纳米材料会表现出特异的光、电、磁、热、力学、机械等性能，纳米技术迅速渗透到材料的各个领域，成为当前世界科学研究的热点。尽管目前纳米技术基本上还处于实验室的初级研究阶段，但毫无疑问，以纳米材料为代表的纳米科技必将对二十一世纪的经济和社会发展产生深刻的影响。对纳米材料的理论研究就显得非常重要。另外，传统的第一性原理方法的计算量比较大，应用到大的纳米或其它体系非常困难，发展计算量小并保持准确性的算法就显得非常重要。本论文共七章，分为两部分：第一部分包括前面五章，主要是应用密度泛函理论研究了各种低维纳米材料特殊的物理化学性质。另外还论及了其它的材料，如硼掺杂的金刚石超导材料。第二部分发展了一些处理大体系的线性标度[O(N)]电子结构方法。

第一章简要介绍了量子化学的历史及发展现状，密度泛函理论的基本框架和近年来的理论发展。密度泛函理论是以基态电子密度为基础，认为一个多粒子体系的任何基态性质都是基态电子密度的函数。密度泛函理论发展的一个主要方向就是寻找合适的交换相关能量泛函。本章最后，我们简要介绍了本论文中所使用的密度泛函计算软件包。

在第二章中，我们主要研究了硼氮纳米管以及氟化的硼氮纳米管。我们讨论了小半径硼氮纳米管的几何、电子、以及振动性质。我们提出了一个生长机制来解释为什么实验上主要合成的是zig–zag型的硼氮纳米管。对于氟化的硼氮纳米管，我们研究了它们的几何结构和电子性质。发现氟原子倾向替代氮原子，导致硼氮层的破坏，但是对电导影响不大。由于氟原子的大的电负性，氟原子更容易吸附在硼原子的顶上。吸附了氟的硼氮纳米管是简并的的半导体，其电导比纯的硼氮纳米管大很多。我们的结果表明实验室合成的氟化的硼氮纳米管极有可能是*p*型的半导体。

第三章预言了两种铁磁半金属低维纳米材料：封装过渡金属纳米线的硼氮纳

米管以及一维的过渡金属苯环三明治高聚物。我们发现所有的过渡金属硼氮纳米管杂化体系都是铁磁金属。Ni纳米线有硼氮纳米管之间的杂化会导致封装Ni纳米线的硼氮纳米管中的半金属或准半金属性。准半金属性的Ni/BN(9,0)是所有Ni/硼氮纳米管中最稳定的杂化结构。通过掺入1.4 *e*/单胞，它可以转变为半金属。有趣的是，我们可以通过对Ni/BN(9,0)施加静压实现准半金属性到半金属的转变。同时调节压力大小，可以调节Ni/BN(9,0)的半金属能隙。另外，被更小BN(8,0)纳米管覆盖的Ni纳米线也是半金属。我们发现这些特殊的磁性质，不只是与Ni纳米线相关的杂化体系才有，其它过渡金属如Fe，Co纳米线/硼氮纳米管的杂化体系也有类似性质。另外，在过渡金属/硼氮纳米管的杂化体系中，自旋以及电子只通过中心的过渡金属纳米线输运，这也与过渡金属/碳纳米管杂化体系不同。我们首次用第一性原理方法研究了一维的$[TM(Bz)]_\infty$（TM=Sc，Ti，V，Cr，和Mn）高聚物的电子及磁性质。结果表明所有的高聚物，除了$[Cr(Bz)]_\infty$，都是金属性的。$[Sc(Bz)]_\infty$是顺磁的，$[Ti(Bz)]_\infty$是磁性的，其中铁磁态与反铁磁态的能量很接近。$[V(Bz)]_\infty$是准半金属性的，$[Mn(Bz)]_\infty$的基态是半金属。另外，$[V(Bz)]_\infty$可以通过拉伸变为半金属。我们研究了由$[V(Bz)]_\infty$和$[Mn(Bz)]_\infty$组成的六角的高聚物束。其中，由于双交换作用，高聚物的链内耦合磁性很大。我们发现高聚物的链间磁性耦合也足够大，可以稳定有限温度下的链内铁磁态。这些特殊的磁性质，使得过渡金属苯环高聚物，尤其$[V(Bz)]_\infty$和$[Mn(Bz)]_\infty$是可能的自旋输运理想材料。

第四章研究了ZnO纳米线的电子，力学，以及压电性质。氧化锌是一种非常重要的材料。由于ZnO纳米线的相对简单的结构以及它的一维特性，并且很多别的ZnO纳米结构也与ZnO纳米线有相似的地方，所以ZnO纳米线的研究就显得特别重要。我们发现由于量子尺寸效应，ZnO纳米线的能隙随着直径减小而单调增大。它们的杨氏模量大于体相的杨氏模量，也是随着直径减小而单调增大。ZnO

纳米线的有效压电常数比体相的大，但是它们不是单调的依赖它们的直径。这是因为两个相反的效应：晶格参数增大和表面原子比例增大。我们的计算结果表明ZnO纳米线应该是很好的纳米传感器。

第五章考察了一些其它体系的性质。其中主要研究了硼掺杂的金刚石超导体的电声耦合。超原胞的计算表明掺杂后金刚石中的光学声子变软。与硼有关的振动模式对于Eliashberg函数有重要贡献。硼掺杂的金刚石中的超导是由于电声耦合机制导致的。通过利用超原胞方法，我们解决了以前理论与实验的矛盾。同时我们计算得到的T_c与实验值非常吻合。

从第六章开始，我们把目光转向研究线性标度的电子结构方法。我们首先回顾了线性标度计算方法的现状。我们首次提出了处理磁性体系的自旋非限制的线性标度的电子结构理论。我们给出了两种分别处理多重度已知和多重度未知的自旋非限制体系的方法。主要基于迹修正方法，我们仔细讨论了我们的方法：PSUTC2和SUTC2。我们发现碳掺杂的BN(7,6)管具有与碳掺杂的BN(5,5)管相似的磁性质。另外，我们发现碳掺杂的硼氮纳米管中的铁磁耦合是不稳定的。利用我们的O(N)方法，处理大的磁性纳米体系将变为可能。最局域化的瓦尼尔函数是理解化学键性质和电子极化，研究弹道输运，强关联电子等的有效工具。我们首次提出了一个线性标度计算最局域化的瓦尼尔函数的方法。我们利用了数值的原子轨道基组而不是通常采用的平面波基组。首先我们利用迹修正方法计算基态的密度矩阵。从这个密度矩阵，我们得到初始的非正交局域轨道。利用修改的Lowdin正交化，我们得到初始的正交原子轨道。由于初始轨道的局域性，Jacobi转动得到最局域化瓦尼尔函数的计算量是O(N)的。我们计算水分子与体相ZnO的结果与别人的计算结果吻合。通过计算硼氮纳米管的最局域化的瓦尼尔函数，可以清楚的看出我们方法的O(N) 行为。我们的新方法提供了一个计算大体系的最局域化的瓦尼尔函数的有效方法，具有广泛的应用前景。最后我们发展了一个简单的计算前线轨道及能隙的线性标度算法。通过与密度矩阵纯化方法或基于局域轨道的线性标度算法连用，它是极好的在自恰的密度泛函理论框架下计算前线轨道的能量及波函数的方法。

在第七章中，我们利用密度矩阵微扰理论来处理周期性体系的响应性质。基于密度矩阵微扰理论，我们把以前计算声子的$O(N^4)$标度减少到O(N)。另外，固体中电场微扰是一个很困难的问题。它的主要困难在于均匀电场产生的静电势$V(\mathbf{r}) = E\,\mathbf{r}$是无界的，而且是和Born-von-Karman周期性边界条件不匹配。我们提出了一个优雅的解决周期体系中均匀电场的办法。与密度矩阵微扰理论结合起来，我们提供了一个计算介电常数的线性标度算法。

关键词：密度泛函理论，纳米材料，线性标度，超导材料

Theoretical Studies of Nano-Materials and Development of Linear Scaling Electronic Structure Methods

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ABSTRACT

With the rapid progress in density functional theory (DFT) and its numerical methods, DFT based first-principles calculation has become a routine method for condensed matter theory, quantum chemistry and material science. Due to the peculiar properties, such as optical, electronic, magnetic, thermal, mechanic properties of nanostructures, nano-materials have attracted much research interest. Although nano-technology is still on elementary stage, nano-technology based on nano-materials will play an important role in modern economy and development in the 21th Century. Theoretical studies are indispensable for understanding the properties of nano-materials and designing novel nano-materials. On the other hand, since traditional first principles methods are computational demanding, thus it is necessary to develop fast especially linear scaling methods. There are two parts in the dissertation: The first part including chapter 1 to chapter 5 focuses on the theoretical studies on various nano-materials. Other materials, for instance boron doped diamond superconductor is also considered. In the second part (chapter 6 and chapter 7), we have developed some linear scaling methods to deal with large scale systems.

In the first chapter, we introduce the basic concept of DFT and review its recent progress. In electron density based DFT, all ground state properties can be derived from the electron density. Finding good approximation for exchange-correlation functional is one of the main targets in DFT. In the last, we introduce briefly the density functional packages used in the current work.

In chapter 2, we focus on boron nitride nanotubes and fluorinated boron nitride nanotubes. The structural, electronic, and vibrational properties of small-radius single-walled BN nanotubes are studied using the density functional method with the local density approximation. The results show that the chirality preference of BN nanotubes observed in experiments may be explained from the relative stability of the corresponding BN strips. Compared with the armchair BN strips, the zigzag BN strips have larger binding energies and thus may be more easily formed. The smallest stable BN nanotube is found to be the (5,0) zigzag nanotube. The energy gap of small zigzag BN nanotubes decreases rapidly with the decrease of radius. The phonon dispersions of BN nanotubes are calculated and the frequency of the radial breathing mode is found to be inversely proportional to the nanotube radius. The structural and electronic properties of fluorine (F)-doped BN nanotubes (BNNTs) are studied using density functional methods. Our results indicate that F atoms prefer to substitute N atoms, resulting in substantial changes of BN layers. However, F substitutional doping results in no shallow impurity states. The adsorption of F atoms on B sites is more stable than that on N sites. BNNTs with adsorbed F atoms are *p*-type

semiconductors, suggesting the electronic conduction in F-doped multiwalled BNNTs with large conductivity observed experimentally might be of *p*-type due to the adsorbed F atoms, but not *n*-type as supposed before.

In chapter 3, we have predicted two kinds of half-metallic ferromagnetic one-dimensional nano-materials: transition-metal encapsulated boron nitride nanotubes and one-dimensional transition metal-benzene sandwich polymers. We have studied zig-zag boron nitride (BN) nanotubes filled with the Ni hexagonal-close-packed nanowire. The Ni/BN nanotube hybrid structures are ferromagnetic metals with substantial magnetism. Some special magnetic properties resulting from the interaction between the Ni nanowire and BN nanotubes are found. The Ni encapsulated BN(9,0) nanotube shows semihalf-metallic behavior, which could become half-metallic after doping electrons more than 1.4 *e*/unit cell. The intrinsic half-metallic behavior could be achieved by two different ways: one is coating the Ni nanowire with a smaller BN nanotube, i.e., BN(8,0), the other is using hydrostatic pressure to homogeneously compress the Ni encapsulated BN(9,0) nanotube. We investigate the electronic and magnetic properties of the proposed one-dimensional transition metal (TM=Sc, Ti, V, Cr, and Mn) -benzene (Bz) sandwich polymers by means of density functional calculations. $[V(Bz)]_\infty$ is found to be a quasi-half-metallic ferromagnet and half-metallic ferromagnetism is predicted for $[Mn(Bz)]_\infty$. Moreover, we show that stretching the $[TM(Bz)]_\infty$ polymers could have dramatic effects on their electronic and magnetic properties. The elongated $[V(Bz)]_\infty$ displays half-metallic behavior, and $[Mn(Bz)]_\infty$ stretched to a certain degree becomes an antiferromagnetic insulator. The possibilities
to stabilize the ferromagnetic order in $[V(Bz)]_\infty$ and $[Mn(Bz)]_\infty$ polymers at finite temperature are discussed. We suggest that the hexagonal bundles composed by these polymers might display intrachain ferromagnetic order at finite temperature by introducing interchain exchange coupling.

In chapter 4, we study the electronic, mechanic, and piezoelectric properties of ZnO nanowires. The band gap, Young's modulus, and piezoelectric constant in nanowires are larger that those in bulk ZnO. The band gaps and Young's modulus of ZnO nanowires increase along with the decrease of the radius of nanowires. Moreover, the piezoelectric constant in nanowires doesn't depend monotonously on the radius of the nanowires due to two competitive effects: elongation of the nanowires and increase of the ratio of surface atoms.

In chapter 5, other materials are examined. We mainly focus on boron doped diamond superconductor. Our supercell calculations indicate the boron-doped diamond is a phonon mediated superconductor, confirming previous theoretical conclusions deduced from the calculations employing the virtual crystal approximation. We show that the optical phonon modes involving B vibrations play an important role in the electron-phonon coupling. Different from previous theoretical results, our calculated electron-phonon coupling constant is 0.39 and the estimated superconducting transition temperature *Tc* is 4.4 K for the boron doped diamond with 2.78% boron content using the Coulomb pseudopotential $\mu^* = 0.10$, in excellent

agreement with the experimental result.

Starting from chapter 6, we begin to focus on the development of linear scaling electronic structure methods. In chapter 6, we first give a brief review of current linear scaling methods. Then we present for the first time the spin-unrestricted linear scaling electronic structure theory. When the spin multiplicity of the system can be predetermined, the generalization of the existing linear scaling methods to spin unrestricted cases is straightforward. However, without calculations it is hard to determine the spin multiplicity of some complex systems, such as, many magnetic nanostructures, some inorganic or bioinorganic molecules. Here we give a general prescription to obtain the spin-unrestricted ground state of open shell systems. Our methods are implemented into the linear scaling trace-correcting density matrix purification algorithm. The numerical atomic orbital basis, rather than the commonly adopted Gaussian basis functions is used. The test systems include O2 molecule, and magnetic carbon doped BN(5,5) and BN(7,6) nanotubes. Using the newly developed method, we find the magnetic moments in carbon doped BN nanotubes couple antiferromagnetically with each other. Our results suggest that the linear scaling spin-unrestricted trace-correcting purification method is very powerful to treat large magnetic systems. We also provide an O(N) method for calculating maximally localized Wannier functions. An O(N) ground state calculation is carried out to get the density matrix (DM) in the atomic orbital basis. Through a projection of the DM onto atomic orbitals and a subsequent O(N) orthogonalization, we obtain initial orthogonal localized orbitals. These orbitals can be maximally localized in linear scaling by simple Jacobi sweeps. Our O(N) method is validated by applying it to water molecule and wurtzite ZnO. The linear scaling behavior of the new method is demonstrated by computing the MLWFs of boron nitride nanotubes. Finally, we propose a simple but effective method to calculate the band edge states in linear scaling. This method is especially suited for getting band edge states in the framework of linear scaling self-consistent density functional or Hartree-Fock theory.

In the last chapter, we employ the density matrix perturbation theory to deal with the response of solid state systems upon various perturbations. We present a method to reduce the computing scaling of the phonon calculation from $O(N^4)$ to O(N). Besides, because the position operator required by the electric field perturbation is ill defined in periodic boundary conditions and unbounded, the behavior of solid state systems upon electric field perturbation is a difficult problem. We propose an O(N) elegant method to calculate dielectric constant by dealing with electric field perturbation in solid through the density matrix perturbation theory.

Keywords: density functional theory; nano-materials, linear-scaling, superconductor