奇偶高次谐波光谱学研究进展

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摘要 不对称分子由于对称破缺在强激光场中会辐射奇次和偶次谐波. 研究表明, 奇偶谐波辐射在频域上具有显著不同的特性. 通过建立奇偶谐波辐射理论模型, 进一步的研究指出, 奇偶谐波携带着系统的不同信息, 可通过提取奇偶谐波各自的特征信息, 整合反演出系统的全部信息. 上述奇偶分辨的高次谐波光谱学研究思路和相关理论模型已被广泛地应用于不对称分子的超快探测过程中, 例如, 可以用于重构不对称分子轨道, 探测极性分子核的动力学, 标定不对称分子取向度, 探测多中心分子结构等; 还可以用于探测不对称分子的形状共振和电荷输运等. 奇偶高次谐波光谱学的研究与发展对推动谐波辐射在阿秒科学和化学反应中的应用发挥着积极作用.

关键词 奇偶谐波辐射, 不对称分子, 超快探测, 阿秒

强激光场中原子分子和固体的高次谐波辐射(high harmonic generation, HHG)是强场物理的研究前沿之一^[1,2], 其在阿秒科学中具有重要应用. 例如, 利用谐波辐射可以在原子时间尺度探测物质结构和电子的动力学^[3,4]、在亚飞秒时间尺度追踪核的运动^[5,6]和监测化学反应中分子键长的变化^[7]等. 基于高次谐波辐射的光谱学新兴学科被称为高次谐波光谱学(high harmonic spectroscopy, HHS).

原子分子谐波辐射的物理机制可通过一个半经典的三步模型^[8]来理解: (1) 束缚电子发生隧穿电离, (2) 电离的电子在激光场中振荡运动, (3) 电离的电子返回母核附近跃迁回到初始态并辐射高能量光子. 先前对于分子谐波辐射的研究集中在对称分子上, 例如Br₂^[7]、N₂^[9-13]、H₂^{+[14-16]}和CO₂^[17]等. 对于这些分子, 一方面由于多核特征, 在强激光作用下会产生准直^[9]和双中心干涉^[14]等效应; 另一方面由于库仑势的对称性, 波函数具有确定宇称, 导致这些分子在单色激光场中通常只辐射奇次谐波.

近期, 人们对分子谐波辐射研究的焦点逐渐移向化学性质更为活泼的不对称分子, 例如HeH₂^{+[18-23]}、CO^[24-32]、HCL^[33]、BF^[34]等. 不同于原子和对称分子, 在强激光作用下不对称分子由于对称破缺会产生一些新的效应, 例如一个激光周期内的不对称电离^[18]. 此外, 由于波函数没有确定宇称, 使得不对称分子在单色激光场中辐射的谐波既包含奇次又包含偶次. 通过将奇次和偶次谐波分开独立研究, 近期的理论工作^[35]指出, 奇偶谐波辐射在频域上具有显著不同的特性. 通过建立奇偶谐波辐射理论模型, 进一步的理论研究^[35,36]表明, 奇偶谐波辐射携带着不对称分子不同的内部结构信息, 并据此提出了针对于不对称分子超快探测的新的光谱学(奇偶高次谐波光谱学)研究思路: 在通过整个谐波谱直接提取不对称系统信息相对困难的情况下, 可将谐波谱中的奇次和偶次谐波解耦, 提取奇、偶谐波各自特征信息, 再整合反演出不对称系统的全部信息.

上述奇偶谐波辐射理论模型的基本假设是(任意不对称波函数总可以分解成偶宇称成分和奇宇称成分之

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和, 下面讨论以不对称轨道中偶宇称成分为主要成分的CO分子为例, 反之亦然: 强激光场中, 不对称轨道的偶宇称成分主导电子隧穿电离(主要路径), 而奇宇称成分的贡献可忽略(次要路径). 由此可以证明, 当电离的电子波包在激光驱动下返回到母核, 与不对称轨道中的偶(奇)宇称成分再结合, 释放奇(偶)次谐波. 因此, 奇次和偶次谐波携带着不同的轨道成分信息. 从鞍点理论出发, 通过理论推导, 相关工作^[37]进一步表明在隧穿电离过程中, 从不对称轨道偶宇称(奇宇称)成分电离的电子波包遭受到了建设性(破坏性)的两中心干涉效应; 而破坏性的干涉效应导致奇宇称成分对电离的贡献可忽略. 这个效应是普遍的, 反映了不对称分子隧穿电离的基本规律——强场电离过程中, 破坏性的分子内部干涉效应将有效抑制不对称轨道中次要成分对电离的贡献. 这个效应也意味着奇偶谐波辐射理论模型具有广泛的适用性. 该理论模型和奇偶分辨的高次谐波光谱学研究思路已被拓展应用于不对称分子超快探测的相关理论研究中, 如重构不对称分子轨道^[36]、探测不对称分子瞬时结构^[38,39]、追踪电子动力学^[40]、探测核的动力学^[41]、标定取向度^[42]、探测多中心分子结构^[43]和探测同位素效应^[44]等.

实验上, 奇偶分辨的高次谐波光谱学研究思路也已被广泛应用于探测不对称分子的结构和内部电子的超快动力学^[45-52]. 相关实验工作进一步表明, 上述奇偶谐波辐射理论模型在考虑取向平均效应后^[42]可用于探测不对称分子的形状共振^[49]和电荷输运^[51,52]等. 最近基于第一性原理计算的理论研究工作也指出上述理论模型的预言与理论计算结果一致^[53]. 下面, 我们具体介绍以该模型为理论工具的奇偶高次谐波光谱学在不对称分子超快探测中的几个应用.

1 重构不对称分子轨道

基于高次谐波辐射的分子轨道层析成像是近些年发展起来的分子轨道超快探测新技术, 在诸如化学反应动力学和原子分子内部电子超快过程探测等方面具有重要的应用. 这一方案是由Itatani等人首次提出并应用于N₂^[9]分子, 随后拓展到CO₂^[17]等分子. 该方案假设仅谐波辐射的再碰撞过程对分子结构响应灵敏且分子轨道波函数具有确定宇称, 这时可以利用取向分子在多周期激光脉冲中的高次谐波辐射来扫描和反演分子轨道. 原始的轨道层析成像方案推广到波函数没有确定宇称的不对称分子时遇到了困难, 需要通过单向再

碰撞方案予以克服^[19,29]. 此时, 还可利用奇偶高次谐波光谱学研究思路, 通过解码不对称分子的奇偶谐波来重构不对称轨道^[36]. 如前所述, 在隧穿区域内, 不对称分子奇(偶)次谐波辐射与不对称分子轨道波函数的偶宇称(奇宇称)成分密切相关. 因此, 从奇(偶)次谐波辐射谱中提取出轨道波函数偶宇称(奇宇称)成分信息, 再通过整合就可以实现不对称分子轨道成像. 图1是利用该方案重构的CO分子的不对称电子轨道. 这一工作为追踪化学反应中中间态的结构提供了思路.

2 探测不对称分子核的动力学

在光诱导化学反应中, 人们渴望能实时观测分子内核的拉伸. 研究人员已经提出了利用谐波辐射实时追踪对称分子(例如Br₂)光解离过程中键长变化的方案^[7]. 对于不对称分子, 其在外场中具有许多新的动力学特性. 关于HeH⁺系统(具有稳定基态的最不对称异核系统, 大爆炸后宇宙中最先合成的化合物)的理论^[41]和实验^[54]工作均表明, 由于固有偶极子导致核的振动态之间直接耦合(直接振动激发通道), 该系统在外场中将在飞秒时间尺度内快速拉伸. 这一极性分子特有的新的拉伸机制与对称分子(例如H₂)在强激光场中的拉伸机制迥异. 外场通常不导致对称分子核振动态之间的耦合, 而仅导致电子态之间的耦合(电子激发通道), 进而引起分子在皮秒时间尺度的拉伸. 进一步的研究表明, HeH⁺系统的谐波辐射主要发生在一关键核间距,

图1 重构不对称分子轨道^[36]. (a) 通过数值方法得到的CO分子的轨道; (b) 通过解码奇偶谐波方案重构的结果

Figure 1 Reconstructing the asymmetric molecular orbital^[36]. (a) The orbital of CO molecule obtained with the numerical method; (b) the reconstruction orbital of CO molecule obtained with the procedure of decoding odd and even harmonics

该关键核间距反映了 HeH^+ 系统的拉伸程度^[41]。利用奇偶高次谐波光谱学研究思路,并借助前述奇偶谐波辐射理论模型,通过对奇偶谐波辐射的极化测量,可提取出关键核间距进而反演飞秒时间尺度内核的运动。如图2(a)~(c),不同取向角下奇偶谐波在垂直箭头处出现交叉,而图2(d)~(f)中只有关键核间距对应的束缚-连续跃迁偶极矩再现了这种交叉现象,即谐波和利用关键核间距计算出来的跃迁偶极矩相互对应。因此,可以利用奇偶谐波来探测关键核间距,进而得到核的拉伸情况。这一工作为实验上实时追踪光化学反应中极性分子键长的变化提供了思路。

3 标定不对称分子取向度

激光诱导分子准直在化学反应动力学、高次谐波光谱学等领域具有广泛的应用。当把这些应用扩展到不对称分子时,除了准直还需要考虑分子的取向问题。但是,在对已经取向不对称分子的光电离或者谐波辐射的相关实验结果进行定量分析之前,如何准确评估取向实验中实现的取向度(degrees of orientation)是需要首先解决的问题。已有研究表明,由于分子结构的影响,不对称分子奇偶谐波辐射在频域和时域均具有不同特性,在基于谐波辐射的不对称分子超快测量实验中,需要充分考虑这些结构造成的差异^[40]。例如,目前

实验中通常利用偶奇率(偶次谐波与奇次谐波的产量比)来标定取向度^[45,46],忽略了不对称分子结构的影响,导致对取向度的评估出现偏差,影响对实验结果的分析。利用奇偶高次谐波光谱学研究思路,通过在奇偶谐波辐射模型中考虑实验因素——取向平均,建立奇偶谐波产量和取向度以及分子结构之间的函数关系,可利用奇偶谐波准确标定不对称分子取向度^[42]。如图3所示,考虑分子结构影响的奇偶高次谐波光谱学标定方案得到的结果(实心符号实线)始终围绕取向度的准确值(虚线),而直接利用偶奇率标定的结果(空心符号虚点线)显著高于准确值,有时甚至大于1(取向度的理论值最大为1)。这一工作为实验上探测不对称分子的取向度提供了思路。

4 探测多中心分子结构

化学反应过程中,多中心分子的核间距可能发生改变。提取核间距的超快变化信息对理解和控制化学反应具有重要意义。近期的理论研究表明,多中心不对称分子奇次谐波和偶次谐波对核间距变化的响应具有显著的差异(图4)^[43]。当相邻核之间的距离发生微小改变时,奇次谐波谱通常不发生改变,而偶次谐波谱变化明显。这种差异是由奇偶谐波不同的发射机制^[36]导致的。当多中心不对称系统中一个原子的位置中心发生微小改

图2 (网络版彩色)探测核的动力学^[41]。不同取向角下, HeH^+ 系统的奇偶谐波谱((a)~(c))与对应的在不同核间距 R 下计算得到的束缚-连续跃迁偶极矩((d)~(f))之间的比较

Figure 2 (Color online) Probing the nuclear dynamics^[41]. Comparisons of odd-even harmonic spectra ((a)~(c)) and bound-continuum transition dipoles ((d)~(f)) of HeH^+ for different angles. The dipoles are calculated using different internuclear distances R

图3 (网络版彩色)标定取向度^[42]。利用不同标定方案得到的针对于不同分子构型的标定结果: 等边三角形((a), (c))和不等边三角形((b), (d))。图中实心符号实线是利用考虑分子结构影响的奇偶高次谐波光谱学标定方案得到的结果; 空心符号虚点线是未考虑分子结构影响直接利用偶奇率标定的结果, 虚线作为基准线表示取向度的准确值

Figure 3 (Color online) Calibrating the degree of orientation^[42]. Results obtained with different calibrating procedures for different molecular configurations: Equilateral triangle ((a), (c)) and scalene triangle ((b), (d)). The curves with solid symbols are the results obtained by using the scheme of odd and even HHS considering the influence of molecular structure, the curves with hollow symbols are the results directly obtained by using the even-odd ratio (without considering the influence of molecular structure), and the short-dashed curves represent the exact results serving as a benchmark

图4 (网络版彩色)探测多中心分子结构^[43]。(I) H_3^{2+} 奇次谐波谱((a), (b))与对应束缚-连续跃迁偶极矩((c), (d))的比较。(II) H_3^{2+} 偶次谐波谱((a), (b))与对应束缚-连续跃迁偶极矩((c), (d))的比较。计算中分子取向角分别为30°((a), (c))和40°((b), (d))。在(I)的第一行(奇次谐波谱)中, 随着核间距变化, 谐波的最小值位置以及谐波相对产量几乎不变, 即奇次谐波对核间距变化的响应不灵敏。在(II)的第一行(偶次谐波谱)中, 随着分子不对称性的增加, 偶次谐波显著增强。各跃迁偶极矩再现了对应谐波的现象

Figure 4 (Color online) Probing the structure of multi-center molecules^[43]. (I) The comparison between the odd harmonic spectra ((a), (b)) and the corresponding bound-continuum transition dipoles ((c), (d)) of H_3^{2+} . (II) The comparison between the even harmonic spectra ((a), (b)) and the corresponding bound-continuum transition dipoles ((c), (d)) of H_3^{2+} . In the calculation, the molecular orientation angles are 30° ((a), (c)) and 40° ((b), (d)), respectively. In the first line (odd harmonic spectra) of (I), with the change of the internuclear distance, the position of the minimum as well as the relative yields of harmonics do not change, that is, the response of odd harmonics to the change of the internuclear distance is not sensitive. In the first line (even harmonic spectra) of (II), with the increase of molecular asymmetry, even harmonics increase significantly. Each transition dipole reproduces the corresponding spectral phenomenon

变时, 不对称轨道的偶宇称成分(再结合过程中主要负责发射奇次谐波)基本不变, 而奇宇称成分(主要负责发射偶次谐波)发生明显改变. 这种差异被清晰地呈现在了奇偶高次谐波谱上. 利用奇偶谐波辐射对核间距变化的不同响应, 借助奇偶谐波辐射理论模型, 可以在超快时间尺度探测多中心分子键长的变化. 这一工作为追踪化学反应中多中心分子核的位置提供了思路.

5 总结

本文介绍了强激光场中不对称分子奇偶谐波辐射

的特性、描述奇偶谐波辐射的理论模型以及奇偶高次谐波光谱学研究思路. 该光谱学研究思路和奇偶谐波辐射理论模型已经被广泛应用于不对称分子超快探测中, 其适用性得到了实验工作及基于第一性原理计算理论工作的支持. 通过几个具体的例子, 我们介绍了如何利用奇偶高次谐波光谱学重构不对称分子轨道、探测极性分子核的动力学、标定不对称分子取向度和探测多中心分子结构等. 奇偶高次谐波光谱学以及相关理论模型将在未来的理论和实验研究中得到进一步的完善和发展, 并拓展新的应用范围.

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Summary for “奇偶高次谐波光谱学研究进展”

Advances on odd-even high-harmonic spectroscopy

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High harmonic generation (HHG) has important applications in attosecond science, such as generating attosecond pulses and probing the structure and the electron dynamics of atoms and molecules with attosecond resolution. Different from symmetric cases, because of symmetry breaking, asymmetric molecules can emit both odd-order and even-order harmonics in strong single-color laser fields. Ultrafast probing of polar molecules with HHG is a hot issue in recent years, as polar molecules are generally very active in chemical reactions. With dividing the HHG signal into odd and even parts, recent studies have shown that odd and even harmonics from asymmetric molecules have different properties in frequency domain. To explain this typical difference, a theoretical model has been developed to describe the generation mechanism of odd versus even HHG from asymmetric molecules. It is shown that during the process of tunneling, the gerade component of the asymmetric orbital plays a dominating role and the contributions of the ungerade component can be neglected. Thereafter, the recombination of the rescattering electron with the gerade (ungerade) component of the asymmetric orbital mainly contributes to the emission of odd (even) harmonics. As a result, odd and even harmonics carry different information of the asymmetric system. Recently, it has been shown that the contributions of the ungerade component of asymmetric orbital to ionization are strongly suppressed due to the destructive intramolecular interference. This suppressing effect is general for strong-field ionization of polar molecules, implying that the theoretical model of odd-even HHG holds for a wide parameter region. These results open a new perspective for probing polar molecules with odd-even HHG. Specifically, when it is relatively difficult to read the information of the molecular structure or the electron dynamics through the whole harmonic spectrum of asymmetric molecules, one can extract the characteristic information of odd or even harmonic separately, then this characteristic information can be integrated and inverted to get the information of the whole asymmetric system. These discussions suggest ultrafast probing of asymmetric molecules with odd-even high-harmonic spectroscopy (HHS), where odd and even harmonics are treated independently. This idea of odd-even HHS and the theoretical model of odd-even HHG mentioned above have been widely used in ultrafast probing of asymmetric molecules in theoretical studies. For example, it has been shown that odd-even HHS and this theoretical model can be used to reconstruct the asymmetric molecular orbital, probe the nuclear dynamics of polar molecules, calibrate the degree of orientation of asymmetric molecules, and probe the structure of multi-center molecules, etc. Experimentally, the idea of odd-even HHS has also been widely used in probing the structure and the electron dynamics of polar molecules. In particular, this theoretical model of odd-even HHG has also been used in probing the shape resonance and charge transport of asymmetric molecules in experiments. In addition, theoretical studies based on the first-principle calculations have also shown the applicability of this theoretical model of odd-even HHG, which provides the theoretical tool for the present odd-even HHS. The research and development of odd-even HHS plays an important role in promoting the application of HHG in attosecond science and chemical reactions.

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