过渡金属配合物非绝热动力学模拟的新进展

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2018-08-30 收稿, 2018-09-22 修回, 2018-09-25 接受, 2018-11-08 网络版发表

国家优秀青年科学基金(21522302)资助

摘要 过渡金属配合物由于其特殊的激发态性质, 在能源、材料、生物等领域有着广阔的应用前景. 对其激发态性质和微观动力学的深入理解不仅需要借助于超快的时间分辨光谱技术, 还需要结合高精度的非绝热动力学模拟. 然而, 由于该类体系激发态比较复杂, 相应的非绝热动力学模拟方法仍有待进一步发展. 为此, 我们简要回顾了目前该类体系非绝热动力学模拟方法的进展与这些方法的一些局限性, 在此基础上, 重点介绍了本课题组所发展并程序化了的一种高效的基于含时密度泛函理论(TD-DFT)的广义最少面跳跃方法. 该方法可以在TD-DFT水平下模拟相同自旋态之间的内转换过程以及不同自旋态之间的系间窜跃过程. 利用新发展的方法, 我们系统地研究了一系列过渡金属配合物超快的激发态动力学过程, 如铈(III)配合物的电子-空穴转移过程, 以及金(I)配合物超快的系间窜跃过程, 模拟结果不仅与已有的实验数据相吻合, 还提供了许多这些超快过程新的机理信息. 该方法的发展为研究过渡金属配合物的激发态动力学提供了强有力的理论模拟工具.

关键词 过渡金属配合物, 非绝热动力学模拟, 广义最少面跳跃方法, 内转换与系间窜跃

过渡金属配合物, 由于其特殊的激发态性质, 在能源^[1~10]、材料^[11~16]及生物^[17~23]等领域有着广阔的应用前景. 在能源领域, 过渡金属配合物可以用于太阳能的转换与存储, 一方面可以用于染料敏化太阳能电池(dye-sensitized solar-cell, DSSC), 直接将太阳能转换为电能; 另一方面也可以利用人工光合作用将太阳能转化为化学能, 从而实现能源的存储与利用^[2~10]. 在材料领域, 利用其发光特性, 可以用于设计具有优异发光性能的有机发光二极管(organic light-emitting diodes, OLED), 还可以利用其非线性光学特性, 实现对入射光的调控^[4,11~16]. 在生物领域, 由于其超快的系间窜跃过程, 可以用于光动力学治疗, 此外, 利用其发光性能, 可以用于生物成像、生物传感器等^[9,17~23]. 然而, 充分利用与调控这些特殊的激发态性质的前提是对其微观机制进行深入细致的理解,

因此, 该类化合物的激发态性质和微观动力学在实验和理论两方面都引起了广泛的研究兴趣^[24~36].

1 研究现状

众所周知, 体系的激发态具有能量高、寿命短的特征, 而过渡金属配合物, 由于过渡金属与配体之间的相互作用, 导致该类体系的激发态特性更加复杂, 种类更多, 如过渡金属与配体之间的电荷转移态(metal-to-ligand charge transfer, MLCT; ligand-to-metal charge transfer, LMCT)、以金属为中心的电子态(metal centered, MC)、配体为中心的电子态(ligand-centered, LC)以及不同配体之间的电荷转移态(ligand-to-ligand charge transfer, LLCT)^[24~28]. 这些不同激发特性的电子态的引入进一步提高了该类化合物激发态动力学过程的复杂性, 其激发态驰豫往往

引用格式: 刘向洋, 崔刚龙. 过渡金属配合物非绝热动力学模拟的新进展. 科学通报, 2018, 63: 3453–3466

Liu X Y, Cui G L. Nonadiabatic dynamics simulation method for transition metal complexes: Theory, developments, and applications (in Chinese). Chin Sci Bull, 2018, 63: 3453–3466, doi: 10.1360/N972018-00897

涉及到内转换、系间窜跃、振动弛豫等多个过程,并伴随着电子转移和空穴转移.这些过程都极大地增加了研究的难度,难以依靠传统的实验手段进行研究,需要借助超快的时间分辨的光谱技术.Vlček等人^[22]和Butler等人^[35]利用时间分辨的红外光谱研究了过渡金属配合物中超快的电子转移过程;Chergui^[36]则利用瞬态吸收光谱、超快荧光上转换和X射线吸收光谱等手段,系统研究了铁、铈、镱、钕、钼等一系列过渡金属配合物超快的内转换、系间窜跃以及振动弛豫过程.通过这些实验手段,已经得到了该类体系激发态失活过程中的许多重要信息.

尽管通过如上所述的实验手段可以得到复杂体系的激发态信息,然而,对光谱信号的解析往往有较大的难度,并且目前的实验手段无法直接在原子级别观测体系的激发态失活过程.因此,如果要准确地得到体系原子级别的激发态动力学过程,需要借助理论计算和模拟.

通过理论计算的手段来研究过渡金属配合物激发态性质的方式大致可分为两类.一种是通过静态电子结构计算,给出激发态势能面的拓扑结构,推测激发态弛豫过程的反应机理和计算相关速率常数^[26-28,32,37-44].然而,如果要研究超快、非平衡的激发态失活过程中的动态信息,如各个光物理和光化学反应过程的时间尺度、反应通道分支比等,静态电子结构的作用有限,需要借助于可靠的非绝热动力学模拟^[45-54].

但是,由于体系复杂、计算昂贵,对于过渡金属配合物超快的非绝热动力学模拟的研究还比较少.值得指出的是,由于动力学过程往往需要大量的电子结构计算,目前仅有基于含时密度泛函(time-dependent density functional theory, TD-DFT)的电子结构计算适用于研究该类体系的激发态动力学行为^[55-60].因此,下面介绍的非绝热动力学方法主要采用含时密度泛函方法进行电子结构计算.

目前,过渡金属配合物的激发态动力学的理论研究主要采用两种方案.(1)基于多组态含时哈特里(multi-configuration time dependent Hartree, MCTDH)的量子动力学方法^[61].Penfold课题组^[46-48]和Daniel课题组^[49,50]利用该方法系统地研究了铈、铁和铜配合物超快的内转换与系间窜跃动力学.该方法可以通过挑选比较重要的振动模式,构造模型哈密顿,从而对体系进行量子动力学模拟.在模型准确的情况下,该

方法可以给出极其准确的动力学结果.该方法主要适用于处理结构变化不大、维度较小、势能面不复杂的光物理动力学过程.对于复杂的体系,谐振子模型和二阶修正的模型不一定能给出准确的描述.此外,对于系间窜跃过程,通常采用Franck-Condon区域计算的旋-轨耦合常数,忽略其动力学效应.(2)非绝热动力学方法则为基于Tully等人^[62,63]提出的面跳跃方法.相对于MCTDH方法,基于面跳跃的方法可以实时地进行全维的动力学模拟,不需要进行振动模式地挑选,也不需要提前拟合势能面或者构造模型哈密顿,然而目前的模拟瓶颈是昂贵的非绝热耦合和旋-轨耦合计算,特别是对于过渡金属配合物(相比于有机体系,更多的激发态需要考虑).

Tavernelli等人^[54]采用最少面跳跃方法在量子力学/分子力学(quantum mechanics/molecular mechanics, QM/MM)级别下研究了铈配合物在水溶液中的激发态动力学过程,然而,由于没有有效的实时计算自旋-轨道耦合的工具,该工作利用轨道对称性,定性地估计了旋-轨耦合的数值,并且使用了精度较低的广义梯度近似泛函, BP86, 而没有使用精度更高的杂化泛函.此外,他们还采用类似的方法研究了铜配合物的光物理过程^[47].此后, González课题组^[51,52]利用他们发展的SHARC程序,也进行了铈配合物激发态动力学的研究.该课题组将SHARC程序接入了ADF软件包中,从而实现了在动力学过程中实时计算自旋-轨道耦合的功能^[51],然而,由于计算昂贵,该方法中依然采用了广义梯度近似泛函PBE,并且模拟的时间也仅有30 fs.对于有着较长时间尺度并需要精度更高的杂化泛函才能较好描述的激发态动力学过程,上述方法仍然难以得到广泛的应用.

综上,如何发展高效的针对过渡金属配合物的非绝热动力学方法是研究过渡金属配合物激发态性质时一个亟待解决的问题.本文中将介绍本课题组最近发展的TD-DFT广义最小面跳跃方法,结合经典路径近似^[64,65],该方法可以准确、高效地模拟过渡金属配合物体系的激发态动力学过程^[66,67].

此外,基于面跳跃方法研究过渡金属的系间窜跃过程,对不同自旋态之间跃迁概率也有着不同的处理方案.Tavernelli等人^[54]采用轨道对称性定性估计自旋-轨道耦合的大小来预估是否发生系间窜跃,或者采用Landau-Zener方法来计算系间窜跃的概率^[47];González课题组^[51,52]则在spin-adiabatic的表象

下计算系间窜跃过程的跃迁概率,但是采取了一些近似;本课题组^[66,67]发展的广义最小面跳跃方法则在spin-diabatic表象下进行工作,采用了近似的有效自旋-轨道耦合来处理系间窜跃过程.

2 广义最少面跳跃方法

由Tully等人^[62,64]发展的最少面跳跃方法和其他的面跳跃方法在研究化学^[66~82],生物^[83~92]和材料^[93~102]等领域超快的激发态过程中已经得到了广泛的应用.基于从头算的方法最小面跳跃方法早期仅适用于研究相同自旋态之间的内转换过程.然而,涉及到不同自旋态的系间窜跃过程,也起着非常重要的作用,尤其是过渡金属配合物.为了同时研究内转换与系间窜跃,一些研究组发展了可以同时研究内转换与系间窜跃过程的面跳跃方法^[71,103~111].下面,将对本课题组^[71]发展的从头算广义最小面跳跃方法作简要介绍.

为了研究不同自旋态之间的系间窜跃过程,我们需要在电子哈密顿算符中包含自旋-轨道耦合相互作用,将自旋-轨道算符作为微扰项加入零级哈密顿量中,得到:

$$\hat{H}(\mathbf{r}, \mathbf{R}(t), s) = \hat{H}_0(\mathbf{r}, \mathbf{R}(t)) + \hat{H}_{so}(\mathbf{r}, s, \mathbf{R}), \quad (1)$$

式中, $\mathbf{r}$ 与 s 分别对应电子的空间坐标与自旋坐标.由此,含时薛定谔方程可以写为如下的形式:

$$i\hbar \dot{\Psi}(\mathbf{r}, \mathbf{R}(t), s, t) = (\hat{H}_0(\mathbf{r}, \mathbf{R}(t)) + \hat{H}_{so}(\mathbf{r}, s, \mathbf{R}(t))) \Psi(\mathbf{r}, \mathbf{R}(t), s, t). \quad (2)$$

而含时的电子波函数可以写作零级绝热电子波函数与相关自旋函数的线性组合:

$$\Psi(\mathbf{r}, \mathbf{R}(t), s, t) = \sum_{i=1}^N c_i(t) \Phi_i^0(\mathbf{r}, \mathbf{R}(t)) \Theta_i(s), \quad (3)$$

式中, $\Theta_i(s)$ 为不含时的自旋函数, $\Phi_i^0(\mathbf{r}, \mathbf{R}(t))$ 为零级哈密顿量在核坐标为 $\mathbf{R}(t)$ 时对应的本征函数解.

将公式(3)代入公式(2),并用 $\Theta_j(s) \Phi_j^0(\mathbf{r}, \mathbf{R}(t))$ 左乘公式后对电子坐标与自旋坐标进行积分,最终可以得到系数演化的方程:

$$\dot{c}_j(t) = -i\hbar^{-1} \left[c_j(t) E_j^0(\mathbf{R}(t)) + \sum_i^N c_i(t) H_{ji}^{so}(\mathbf{R}(t)) \right] - \sum_i^N c_i(t) \Lambda_{ji}(t) \langle \Theta_j(s) | \Theta_i(s) \rangle. \quad (4)$$

$H_{ji}^{so}(\mathbf{R}(t)) = \langle \Theta_j(s) \Phi_j^0(\mathbf{r}, \mathbf{R}(t)) | \hat{H}_{so}(\mathbf{r}, s, \mathbf{R}(t)) | \Phi_i^0(\mathbf{r}, \mathbf{R}(t)) \Theta_i(s) \rangle$ 为电子态 j 和电子态 i 在核坐标为 $\mathbf{R}(t)$ 时对应的

自旋-轨道耦合矩阵元.而 $\Lambda_{ji}(t) = \mathbf{v}(t) \cdot \mathbf{d}_{ji}(\mathbf{R}(t))$ 则为电子态之间的非绝热耦合项.式(4)即为广义最小面跳跃方法对应的主要方程,利用该公式即可同时研究相同自旋与不同自旋之间的非辐射跃迁过程.

在广义最小面跳跃方法中,最小面跳跃的跃迁概率的计算公式需要在原有公式的基础上考虑旋-轨耦合的贡献.采用与Tully等人^[62,63]类似的方法进行推导,最终得到如下的由电子态 i 到电子态 j 的跃迁概率计算公式:

$$p_{ij}(t) dt = 2 \frac{\text{Re}(c_i^* c_j \Lambda_{ij}) - \text{Im}(\hbar^{-1} c_i^* c_j H_{ij}^{so})}{c_i^* c_i} dt. \quad (5)$$

通过上述的公式可以看出,在求解系数演化方程中,如何高效地计算相同自旋态之间的非绝热耦合项,以及不同自旋态之间的自旋-轨道耦合,是提高从头算非绝热动力学模拟效率的关键所在.

在TD-DFT框架下,目前有两种计算非绝热耦合项的数值算法^[112~114].一种是Pittner等人^[112]和Tapavicza等人^[113]采用的基于Slater行列式的计算方法;另一种为最近Izmaylov课题组^[114]提出的基于分子轨道的计算方法.相对于基于Slater行列式的数值算法,基于分子轨道的数值算法更为高效,测试体系显示可以达到几百甚至上千倍的加速.在广义最小面跳跃方法中,主要采用基于分子轨道的数值算法计算非绝热耦合项.对于TD-DFT级别下旋-轨耦合,也有多种计算方法^[115].本文的应用例子中主要用ADF软件包来进行旋-轨耦合计算^[116~122].独立的TD-DFT级别的旋-轨耦合计算模块也已经完成,在下阶段的工作中将会介绍.

3 应用举例

利用新发展的TD-DFT级别的广义最少面跳跃方法研究了一些重要的过渡金属配合物的超快激发态弛豫过程,如铈(III)配合物的早期的激发态动力学行为,以及金(I)配合物的超快系间窜跃过程.下面分别对上述的两个体系做简要介绍.

值得强调的是,由于TD-DFT方法计算得到的能量等性质与泛函的选取密切相关,在进行计算模拟之前需要进行大量的测试来选取合适的泛函和基组.我们主要通过计算并拟合吸收光谱并与实验中已有的吸收光谱进行比较,从而确定适用于不同体系的泛函和基组.对于铈(III)配合物体系,采用B3LYP泛

函^[123-126], 对铱原子采用LANL2DZ赝势基组^[127], 对其余非金属元素采用6-31G(d)基组, 结果与实验中的吸收光谱吻合的比较好^[128,129]; 而对于金(I)配合物体系, 采用CAM-B3LYP泛函^[130]对金原子采用LANL2DZ赝势基组^[127], 对其余非金属元素采用cc-pVDZ基组则与实验中的吸收光谱吻合的很好^[131]. 因此在动力学模拟过程中, 分别采用如上所述泛函和基组, 使用GAUSSIAN09软件包完成除自旋-轨道耦合外其他物理量的计算^[132]. 后期工作已经完全采用GAUSSIAN09软件来处理, 经前期测试, 两种方法可以给出一致的结果. 具体的计算细节可参考文献[66,67], 在本文中不再赘述.

在动力学模拟的过程中, 往往还需要选取初始电子态. 体系受光激发后, 体系主要激发至激发单重态. 一般根据实验中的激发波长, 选取相应的激发单重态作为动力学模拟的初始态, 并同时包含在该初始态之下和接近的所有激发单重态和三重态. 对铱(III)配合物体系, 包含了稍多的激发态三重态, 模拟结果表明, 能量高于初始激发单重态的三重态对激发态动力学的影响微乎其微. 因此, 按上述方案选取合适数量的激发三重态即可, 包含更多的激发三态对动力学影响不大.

3.1 不同配体铱(III)配合物的超快动力学

由于在OLED领域有着巨大的应用前景, 铱(III)配合物的激发态性质以及光物理过程获得了理论与实验的广泛关注^[133-143]. 通过改变配体的结构, 可以调节铱(III)配合物激发态性质, 从而实现不同的发光性能. 最近, Pomarico等人^[139]采用飞秒级别的发光上转换光谱系统地研究了一系列不同配体的铱(III)配合物的激发态动力学. 然而, 对于该类化合物激发态的非绝热动力学模拟的研究仍是一片空白. 为了填补这一空白和研究其光物理机制, 本课题组^[66]首次采用发展的从头算非绝热动力学模拟方法, 系统地研究了图1所示3个不同配体的铱(III)配合物的激发态动力学.

在非绝热动力学模拟中包含了实验中激发光谱范围内的5个激发单重态 $S_n(n=1\sim5)$, 以及10个激发三重态 $T_n(n=1\sim10)$. 不同配体铱(III)配合物的光物理过程如图2所示. 可以看出对于3个铱(III)配合物, 从 S_n 到 T_n 有着超快的系间窜跃过程, 模拟得到的系间窜跃的速率分别为65, 81, 140 fs, 与实验值80, 80, 110 fs非常接近. 此外, 单重激发态与三重激发态各自的内

图1 不同配体的含铱(III)配合物的结构示意图, 分别记为Ir1(a), Ir2(b), Ir3(c). ppy, bpy, ppz和dipy分别表示不同的配体结构

Figure 1 Three Ir-containing molecular systems studied in this work, which are referred to as Ir1 (a), Ir2 (b), and Ir3 (c). Also shown are their ppy, bpy, ppz, and dipy ligands

转换过程也是超快的. 体系较大的非绝热耦合与旋-轨耦合数值, 以及激发态之间较小的能量差是造成这一超快现象的本质原因.

值得指出的是, 尽管这些配合物在宏观上都表现出了超快的内转换与系间窜跃过程, 但是对于不同配体的配合物, 其微观的弛豫过程却是迥异的. 首先, 弛豫过程不同, 对于Ir1, 体系在超快地系间窜跃至三重态空间后, 很快失活至 T_1 态; 对于Ir2, 系间窜跃至三重态空间后, 先超快弛豫至 T_2 态, 之后再通过系间窜跃弛豫至 S_1 态, 最终才到达 T_1 态; 而Ir3在弛豫至三重态空间后, 先到达 T_2 态, 并在 T_2 态停留一段时间后, 最终回到 T_1 态. 此外, 其电子与空穴转移过程也不尽相同: 对Ir1, 在激发态弛豫过程中, 主要发生中心Ir原子到ppy配体的空穴转移, 而整个弛豫过程中的电子转移几乎可以忽略不计; 对于Ir2, 主要发生的则是在ppy配体与bpy配体之间的电荷转移, 而仅有一小部分空穴从Ir原子转移到了ppy配体上; 对于Ir3, 则同时发生从ppz配体到dipy配体的电子与空穴转移.

综上, 非绝热动力学模拟成功地揭示出了不同配体如何调控铱(III)配合物的激发态动力学的微观过程, 并合理地解释了实验中的新奇现象^[139]. 这些激发态动力学信息对于设计发光性能更加优越的新型铱(III)配合物提供了重要的理论参考.

3.2 不同位置取代基金(I)配合物超快的系间窜越

金(I)配合物通过与碳原子形成 σ 键, 可以显著地

图2 (网络版彩色)非绝热动力学模拟得到的Ir1(a), Ir2(b), Ir3(c)激发态失活机理及电子、空穴转移过程示意图

Figure 2 (Color online) Excited-state relaxation mechanisms of Ir1 (a), Ir2 (b), and Ir3 (c) and their hole and electron transfer processes based on our present nonadiabatic dynamics simulations

改变原碳氢化合物的电子态性质,从而调控体系的光物理与光化学过程^[144~161].然而,相对于对该类化合物吸收与发射光谱性质的研究,其激发态动力学的理论研究很少报道.最近,Crespo-Hernández课题组^[160]利用瞬态吸收光谱以及简单的电子结构计算,研究了如图3所示3个类似的金(I)配合物(实验中的环己基,理论计算模型中用甲基代替)的激发态弛豫机理.研究发现尽管该类化合物都有着超快的系间窜跃过程,时间尺度均在350 fs以内,但该类物质的激发态动力性质与萘环上的取代基有着一定的关系:(1) 对比Au1和Au2,在增加第2个含金取代基并没有显著增强体系的系间窜跃速率;(2) 对比Au2和Au3,第2个取代基的位置对体系的系间窜跃速率有着显著的影响,Au2的系间窜跃速率比Au3慢了3倍.实验中利用费米黄金规则定性地推测了造成这一现象的可能原因.然而,其微观机制仍然不清楚,为此,本课题组^[67]采用从头算非绝热动力学模拟,在TD-DFT级

图3 (网络版彩色)模拟研究的3个不同的金(I)配合物模型,分别记为Au1(a), Au2(b), Au3(c)

Figure 3 (Color online) Three Au-containing molecular systems studied in this work, which are referred to as Au1 (a), Au2 (b), and Au3 (c)

别研究了3个金(I)化合物超快的系间窜跃过程.

与之前铱(III)配合物的模拟过程类似,依据实验中的激发波长,在非绝热动力学模拟中包含了1个激发单重态以及5个激发三重态,根据模拟的结果,总结出如图4所示的机理图.可以看出,在激发至 S_1 态后,3个体系都以超快的速度系间窜跃至激发三重态,

图4 (网络版彩色)非绝热动力学模拟得到的Au1(a), Au2(b), Au3(c)体系的激发态弛豫动力学机理

Figure 4 (Color online) Excited-state relaxation mechanisms of Au1 (a), Au2 (b), and Au3 (c) based on our present nonadiabatic dynamics simulations

系间窜跃的时间尺度分别为317, 489以及164 fs, 与实验中测得的系间窜跃速率230, 330, 100 fs物理趋势一致, 存在一个简单ln2的倍数关系, 说明了模拟结果的可靠性. 进一步分析各个体系的系间窜跃过程, 发现这3个体系虽然都主要通过 S_1 系间窜跃至 T_4 , T_5 态. 然而, 不同体系在这两个态跃迁的比例不尽相同. Au1和Au2主要跃迁至 T_5 态, 比例分别为66.2%和53.6%, 少部分跃迁至 T_4 态, 比例为19.2%和20.6%; 而Au3则在 T_5 和 T_4 态的跃迁接近, T_5 态所占的比例稍多一些, 分别为48.8%与34.6%.

由于系间窜跃过程与电子态之间的能量差与旋-轨耦合相关, 为了进一步理解造成上述激发态弛豫过程的原因, 分析了不同体系的电子态之间的能量差以及旋-轨耦合. 表1列出了Au1, Au2, Au3的 S_1 态与相近的 T_5 , T_4 , T_3 态的平均能量差, 表2则列出了3个体系 S_1 态与 T_5 , T_4 , T_3 态的平均自旋-轨道耦合.

分析表1和2的数据可以看出, 对于Au1与Au2, S_1 与 T_5 的能量差分别为2.51和1.47 kcal/mol, 明显小于 S_1 与 T_4 态的能量差, 5.08 vs. 3.71 kcal/mol, 而相应的旋-轨耦合, 两个体系也均是 S_1/T_5 的自旋-轨道耦合稍大些, Au1, 137 vs. 85 cm^{-1} , Au2, 58 vs. 54 cm^{-1} , 两

表1 Au1, Au2, Au3 体系 S_1 态与 T_5 , T_4 , T_3 态的平均能量差

Table 1 Averaged energy gaps (in kcal/mol) between S_1 and T_n ($n=5-3$) states in dynamics simulations of Au1, Au2, and Au3

平均能量差 (kcal/mol)	Au1	Au2	Au3
$ S_1-T_5 $	2.51	1.47	2.29
$ S_1-T_4 $	5.08	3.71	2.90
$ S_1-T_3 $	8.04	6.33	5.89

方面的原因共同造成了Au1与Au2均主要跃迁至 T_5 态, 少部分跃迁至 T_4 态. 而进一步对比这两个体系, 尽管Au2的能量差略小于Au1, 其自旋-轨道耦合却也远小于Au1, 总体导致Au2的系间窜跃速率略小于Au1, 489 vs. 317 fs. 而对于Au3, 可以发现该体系的 S_1 态与 T_5 , T_4 态的能量均很接近, 2.29 vs. 2.90 kcal/mol, 且自旋-轨道耦合都比较大, 100 vs. 79 cm^{-1} , 因此与Au2对比, Au3有 $S_1 \rightarrow T_5$ 和 $S_1 \rightarrow T_4$ 两条主要的弛豫通道, 并且该体系的自旋-轨道耦合也远大于Au2, 最终造成了Au3的系间窜跃速率相比Au2快了3倍, 164 vs. 489 fs. 与Au1相比, 尽管Au1的自旋-轨道耦合相对较大, 但由于Au3的多条弛豫通道以及较小的能量差, 导致Au3的系间窜跃速率略快于Au1, 164 vs. 317 fs.

表 2 Au1, Au2, Au3 体系 S_1 态与 T_5 , T_4 , T_3 态的平均自旋-轨道耦合(cm^{-1})

Table 2 Averaged spin-orbit couplings (in cm^{-1}) between the S_1 and T_n ($n=3, 4, 5$) states in dynamics simulations of Au1, Au2, and Au3

	Au1	Au2	Au3
S_1/T_5	137	58	100
S_1/T_4	85	54	79
S_1/T_3	89	38	67

综上所述,本课题组^[160]在TD-DFT级别采用了非绝热动力学模拟,系统研究了3个含金化合物超快的系间窜跃过程,除了与实验结果吻合的较好外,我们还得到了一些新的机理信息。(1)造成这类体系超快系间窜跃过程是 S_1 态与 T_n 态间较小的能量差与较大的自旋-轨道耦合共同作用的结果;(2)与预期相反,增加第2个含金取代基并没有增加,反而减小了体系的自旋-轨道耦合,这说明重原子效应并不是普适的,与体系几何结构和激发态的电子结构有着密切相关^[162];(3)第2个取代基引入的位置可以显著影响体系的电子结构,并最终导致体系不同的系间窜

跃速率。这些新的机理信息有助于我们进一步设计有特殊性质金(I)配合物。

4 总结

过渡金属配合物的非绝热动力学模拟对于理解该类化合物的特殊的激发态性质有着重要的意义,然而,由于体系复杂,相关的模拟方法仍有待进一步发展。为此,我们发展了基于TD-DFT方法的广义最小面跳跃方法,该方法可以同时用于研究相同自旋态之间的内转换过程与不同自旋态之间的系间窜跃过程,并且,相对于早期的算法,大大减少了计算量,适用于研究复杂的过渡金属配合物体系。为了证明方法的有效性,我们系统地研究了铈(III)配合物以及金(I)配合物超快的激发态动力学过程,相关的模拟结果不仅与已有的实验数据相吻合,还提供了许多新的机理信息,证明了我们发展的方法的可靠性和准确性。该方法为研究过渡金属配合物的激发态性质提供了强有力的理论工具。合理地考虑环境效应和进一步优化算法提高计算模拟精度和效率是下一步的发展方向。

参考文献

- Garino C, Salassa L. The photochemistry of transition metal complexes using density functional theory. *Philos Trans Royal Soc A*, 2013, 371: 20120134
- Grätzel M. Dye-sensitized solar cells. *J Photochem Photobiol C*, 2003, 4: 145–153
- Polo A S, Itokazu M K, Iha N Y M. Metal complex sensitizers in dye-sensitized solar cells. *Coord Chem Rev*, 2004, 248: 1343–1361
- Fantacci S, De Angelis F. A computational approach to the electronic and optical properties of Ru(II) and Ir(III) polypyridyl complexes: Applications to DSC, OLED and NLO. *Coord Chem Rev*, 2011, 255: 2704–2726
- Jäger M, Freitag L, González L. Using computational chemistry to design Ru photosensitizers with directional charge transfer. *Coord Chem Rev*, 2015, 304: 146–165
- Gust D, Moore T A, Moore A L. Solar fuels via artificial photosynthesis. *Acc Chem Res*, 2009, 42: 1890–1898
- Teets T S, Nocera D G. Photocatalytic hydrogen production. *Chem Commun*, 2011, 47: 9268–9274
- Hennig H, Belle M, Bolm C. Transition Metals in Photocatalysis. Weinheim: Wiley-VCH Verlag GmbH, 2008
- Bitterwolf T. Photochemistry of Transition Metal Complexes. Hoboken, New Jersey: John Wiley & Sons Ltd., 2011
- Twilton J, Le C, Zhang P, et al. The merger of transition metal and photocatalysis. *Nat Rev Chem*, 2017, 1: Unsp0052
- Choy W C H, Chan W K, Yuan Y. Recent advances in transition metal complexes and light-management engineering in organic optoelectronic devices. *Adv Mater*, 2014, 26: 5368–5399
- Yersin H, Rausch A F, Czerwieniec R, et al. The triplet state of organo-transition metal compounds. Triplet harvesting and singlet harvesting for efficient OLEDs. *Coord Chem Rev*, 2011, 255: 2622–2652
- Powell B J. Theories of phosphorescence in organo-transition metal complexes-from relativistic effects to simple models and design principles for organic light-emitting diodes. *Coord Chem Rev*, 2015, 295: 46–79
- Zhang J, Chu B W K, Zhu N, et al. Synthesis, characterization, langmuir-blodgett film-forming property, and second-order nonlinear optical study of rhenium(I) and ruthenium(II) diimine complexes. *Organometallics*, 2007, 26: 5423–5429
- Coppens P, Novozhilova I, Kovalevsky A. Photoinduced linkage isomers of transition-metal nitrosyl compounds and related complexes. *Chem Rev*, 2002, 102: 861–883
- Polo A S, Itokazu M K, Frin K M, et al. Light driven trans-to-cis isomerization of stilbene-like ligands in *fac*-[Re(CO)₃(NN)(*trans*-L)]⁺

- and luminescence of their photoproducts. *Coord Chem Rev*, 2006, 250: 1669–1680
- 17 Farrer N J, Salassa L, Sadler P J. Photoactivated chemotherapy (PACT): The potential of excited-state d-block metals in medicine. *Dalton Trans*, 2009, (48): 10690–10701
- 18 Dolmans D E J G J, Fukumura D, Jain R K. Photodynamic therapy for cancer. *Nat Rev Cancer*, 2003, 3: 380
- 19 Ruggi A, van Leeuwen F W B, Velders A H. Interaction of dioxygen with the electronic excited state of Ir(III) and Ru(II) complexes: Principles and biomedical applications. *Coord Chem Rev*, 2011, 255: 2542–2554
- 20 Lakowicz J R. *Principles of Fluorescence Spectroscopy*. Baltimore: Springer, 2006
- 21 Gray H B, Winkler J R. Electron tunneling through proteins. *Q Rev Biophys*, 2003, 36: 341–372
- 22 Vlček A Jr, Kvapilová H, Towrie M, et al. Electron-transfer acceleration investigated by time resolved infrared spectroscopy. *Acc Chem Res*, 2015, 48: 868–876
- 23 Fernández-Moreira V, Thorp-Greenwood F L, Coogan M P. Application of d^6 transition metal complexes in fluorescence cell imaging. *Chem Commun*, 2010, 46: 186–202
- 24 Turki M, Daniel C, Zális S, et al. UV-visible absorption spectra of $[\text{Ru}(\text{E})(\text{E}')(\text{CO})_2(\text{iPr-DAB})]$ ($\text{E}=\text{E}'=\text{SnPh}_3$ or Cl ; $\text{E}=\text{SnPh}_3$ or Cl , $\text{E}'=\text{CH}_3$; $\text{iPr-DAB}=\text{N,N'}$ -Di-isopropyl-1,4-diaza-1,3-butadiene): Combination of CASSCF/CASPT2 and TD-DFT calculations. *J Am Chem Soc*, 2001, 123: 11431–11440
- 25 Daniel C. Electronic spectroscopy and photoreactivity in transition metal complexes. *Coord Chem Rev*, 2003, 238: 143–166
- 26 Daniel C. Photochemistry and photophysics of transition metal complexes: Quantum chemistry. *Coord Chem Rev*, 2015, 282: 19–32
- 27 Daniel C. *Absorption Spectroscopy, Emissive Properties, and Ultrafast Intersystem Crossing Processes in Transition Metal Complexes: TD-DFT and Spin-orbit Coupling*. Cham: Springer International Publishing, 2016
- 28 Daniel C, Gourlaouen C. Chemical bonding alteration upon electronic excitation in transition metal complexes. *Coord Chem Rev*, 2017, 344: 131–149
- 29 Vlček A. *Ultrafast Excited-state Processes in Re(I) Carbonyl-diimine Complexes: From Excitation to Photochemistry*. Berlin, Heidelberg: Springer, 2009
- 30 Kumar A, Sun S S, Lees A J. *Photophysics and photochemistry of organometallic rhenium diimine complexes*. Berlin, Heidelberg: Springer, 2010
- 31 Wagenknecht P S, Ford P C. Metal centered ligand field excited states: Their roles in the design and performance of transition metal based photochemical molecular devices. *Coord Chem Rev*, 2011, 255: 591–616
- 32 Baryshnikov G, Minaev B, Ågren H. Theory and calculation of the phosphorescence phenomenon. *Chem Rev*, 2017, 117: 6500–6537
- 33 Sone K, Fukuda Y. Solvatochromism of transition metal complexes with organic ligands in donor and acceptor solvents. *Rev Inorg Chem*, 1990, 11: 123–153
- 34 Lees A J. The luminescence rigidochromic effect exhibited by organometallic complexes: Rationale and applications. *Comments Inorg Chem*, 1995, 17: 319–346
- 35 Butler J M, George M W, Schoonover J R, et al. Application of transient infrared and near infrared spectroscopy to transition metal complex excited states and intermediates. *Coord Chem Rev*, 2007, 251: 492–514
- 36 Chergui M. Ultrafast photophysics of transition metal complexes. *Acc Chem Res*, 2015, 48: 801–808
- 37 Mai S, Plasser F, Dorn J, et al. Quantitative wave function analysis for excited states of transition metal complexes. *Coord Chem Rev*, 2018, 361: 74–97
- 38 González L, Escudero D, Serrano-Andres L. Progress and challenges in the calculation of electronic excited states. *ChemPhysChem*, 2012, 13: 28–51
- 39 Vancoillie S, Zhao H, Van Tan T, et al. Multiconfigurational second-order perturbation theory restricted active space (RASPT2) studies on mononuclear first-row transition-metal systems. *J Chem Theory Comput*, 2011, 7: 3961–3977
- 40 Dreuw A, Head-Gordon M. Single-reference *ab initio* methods for the calculation of excited states of large molecules. *Chem Rev*, 2005, 105: 4009–4037
- 41 Labat F, Le Bahers T, Ciofini I, et al. First-principles modeling of dye-sensitized solar cells: Challenges and perspectives. *Acc Chem Res*, 2012, 45: 1268–1277
- 42 Adamo C, Jacquemin D. The calculations of excited-state properties with time-dependent density functional theory. *Chem Soc Rev*, 2013, 42: 845–856
- 43 Alary F, Boggio-Pasqua M, Heully J L, et al. Theoretical characterization of the lowest triplet excited states of the tris-(1,4,5,8-tetraazaphenanthrene) ruthenium dication complex. *Inorg Chem*, 2008, 47: 5259–5266
- 44 Heully J L, Alary F, Boggio-Pasqua M. Spin-orbit effects on the photophysical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$. *J Chem Phys*, 2009, 131: 184308

- 45 Tavernelli I. Nonadiabatic molecular dynamics simulations: Synergies between theory and experiments. *Acc Chem Res*, 2015, 48: 792–800
- 46 Capano G, Chergui M, Rothlisberger U, et al. A quantum dynamics study of the ultrafast relaxation in a prototypical Cu(I)-phenanthroline. *J Phys Chem A*, 2014, 118: 9861–9869
- 47 Capano G, Penfold T J, Chergui M, et al. Photophysics of a copper phenanthroline elucidated by trajectory and wavepacket-based quantum dynamics: A synergetic approach. *Phys Chem Chem Phys*, 2017, 19: 19590–19600
- 48 Pápai M, Vankó G, Rozgonyi T, et al. High-efficiency iron photosensitizer explained with quantum wavepacket dynamics. *J Phys Chem Lett*, 2016, 7: 2009–2014
- 49 Harabuchi Y, Eng J, Gindensperger E, et al. Exploring the mechanism of ultrafast intersystem crossing in rhenium(I) carbonyl bipyridine halide complexes: Key vibrational modes and spin-vibronic quantum dynamics. *J Chem Theory Comput*, 2016, 12: 2335–2345
- 50 Fumanal M, Gindensperger E, Daniel C. Ultrafast excited-state decays in $[\text{Re}(\text{CO})_3(\text{N},\text{N})(\text{L})]^{n+}$: Nonadiabatic quantum dynamics. *J Chem Theory Comput*, 2017, 13: 1293–1306
- 51 Atkins A J, González L. Trajectory surface-hopping dynamics including intersystem crossing in $[\text{Ru}(\text{bpy})_3]^{2+}$. *J Phys Chem Lett*, 2017, 3840–3845
- 52 Freitag L, González L. Theoretical spectroscopy and photodynamics of a ruthenium nitrosyl complex. *Inorg Chem*, 2014, 53: 6415–6426
- 53 Moret M E, Tavernelli I, Chergui M, et al. Electron localization dynamics in the triplet excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ in aqueous solution. *Chem Eur J*, 2010, 16: 5889–5894
- 54 Tavernelli I, Curchod B F E, Rothlisberger U. Nonadiabatic molecular dynamics with solvent effects: A LR-TDDFT QM/MM study of ruthenium(II) tris(bipyridine) in water. *Chem Phys*, 2011, 391: 101–109
- 55 Hohenberg P, Kohn W. Inhomogeneous electron gas. *Phys Rev B*, 1964, 136: B864–B871
- 56 Kohn W, Sham L J. Self-consistent equations including exchange and correlation effects. *Phys Rev*, 1965, 140: A1133–A1138
- 57 Becke A D. Density-functional thermochemistry .3. The role of exact exchange. *J Chem Phys*, 1993, 98: 5648–5652
- 58 Runge E, Gross E K U. Density-functional theory for time-dependent systems. *Phys Rev Lett*, 1984, 52: 997–1000
- 59 Petersilka M, Gossmann U J, Gross E K U. Excitation energies from time-dependent density-functional theory. *Phys Rev Lett*, 1996, 76: 1212–1215
- 60 Casida M E, Huix-Rotllant M. Progress in time-dependent density-functional theory. *Ann Rev Phys Chem*, 2012, 63: 287–323
- 61 Beck M H, Jäckle A, Worth G A, et al. The multiconfiguration time-dependent hartree (MCTDH) method: A highly efficient algorithm for propagating wavepackets. *Phys Rep*, 2000, 324: 1–105
- 62 Hammes-Schiffer S, Tully J C. Proton-transfer in solution-molecular-dynamics with quantum transitions. *J Chem Phys*, 1994, 101: 4657–4667
- 63 Tully J C, Preston R K. Trajectory surface hopping approach to nonadiabatic molecular collisions—Reaction of H^+ with D_2 . *J Chem Phys*, 1971, 55: 562–572
- 64 Akimov A V, Neukirch A J, Prezhdo O V. Theoretical insights into photoinduced charge transfer and catalysis at oxide interfaces. *Chem Rev*, 2013, 113: 4496–4565
- 65 Zheng Q, Xie Y, Lan Z, et al. Phonon-coupled ultrafast interlayer charge oscillation at van der Waals heterostructure interfaces. *Phys Rev B*, 2018, 97: 205417
- 66 Liu X Y, Zhang Y H, Fang W H, et al. Early-time excited-state relaxation dynamics of iridium compounds: Distinct roles of electron and hole transfer. *J Phys Chem A*, 2018, 122: 5518–5532
- 67 Liu X Y, Li Z W, Fang W H, et al. Nonadiabatic dynamics simulations on internal conversion and intersystem crossing processes in gold(I) compounds. *J Chem Phys*, 2018, 149: 044301
- 68 Cui G L, Thiel W. Generalized trajectory surface-hopping method for internal conversion and intersystem crossing. *J Chem Phys*, 2014, 141: 124101
- 69 Cui G L, Fang W H. *Ab initio* trajectory surface-hopping study on ultrafast deactivation process of thiophene. *J Phys Chem A*, 2011, 115: 11544–11550
- 70 Cui G L, Thiel W. Photoinduced ultrafast Wolff rearrangement: A non-adiabatic dynamics perspective. *Angew Chem Int Ed*, 2013, 52: 433–436
- 71 Cui G L, Fang W H. *Ab initio* based surface-hopping dynamics study on ultrafast internal conversion in cyclopropanone. *J Phys Chem A*, 2011, 115: 1547–1555
- 72 Xia S H, Liu X Y, Fang Q, et al. Photodissociation dynamics of $\text{CH}_3\text{C}(\text{O})\text{SH}$ in argon matrix: A QM/MM nonadiabatic dynamics simulation. *J Chem Phys*, 2015, 143: 194303
- 73 Xia S H, Xie B B, Fang Q, et al. Excited-state intramolecular proton transfer to carbon atoms: Nonadiabatic surface-hopping dynamics simulations. *Phys Chem Chem Phys*, 2015, 17: 9687–9697

- 74 Wang Y T, Liu X Y, Cui G L, et al. Photoisomerization of arylazopyrazole photoswitches: Stereospecific excited-state relaxation. *Angew Chem Int Ed*, 2016, 55: 14009–14013
- 75 Liu X Y, Fang Y G, Xie B B, et al. QM/MM nonadiabatic dynamics simulations on photoinduced Wolff rearrangements of 1,2,3-thiadiazole. *J Chem Phys*, 2017, 146: 224302
- 76 Xie B B, Liu X Y, Fang Q, et al. The position of the N atom plays a significant role for excited-state decay of heterocycles. *J Phys Chem Lett*, 2017, 8: 1019–1024
- 77 Weingart O, Lan Z, Koslowski A, et al. Chiral pathways and periodic decay in *cis*-azobenzene photodynamics. *J Phys Chem Lett*, 2011, 2: 1506–1509
- 78 Fischer S A, Chapman C T, Li X. Surface hopping with ehrenfest excited potential. *J Chem Phys*, 2011, 135: 144102
- 79 Yu L, Xu C, Lei Y, et al. Trajectory-based nonadiabatic molecular dynamics without calculating nonadiabatic coupling in the avoided crossing case: *Trans*↔*cis* photoisomerization in azobenzene. *Phys Chem Chem Phys*, 2014, 16: 25883–25895
- 80 Yu L, Xu C, Zhu C. Probing the $\pi \rightarrow \pi^*$ photoisomerization mechanism of *cis*-azobenzene by multi-state *ab initio* on-the-fly trajectory dynamics simulation. *Phys Chem Chem Phys*, 2015, 17: 17646–17660
- 81 Gao A H, Li B, Zhang P Y, et al. Nonadiabatic *ab initio* molecular dynamics of photoisomerization in bridged azobenzene. *J Chem Phys*, 2012, 137: 204305
- 82 Guo X, Zhao Y, Cao Z. A QM/MM MD insight into photodynamics of hypoxanthine: Distinct nonadiabatic decay behaviors between keto-N₇H and keto-N₉H tautomers in aqueous solution. *Phys Chem Chem Phys*, 2014, 16: 15381–15388
- 83 Cui G L, Lan Z, Thiel W. Intramolecular hydrogen bonding plays a crucial role in the photophysics and photochemistry of the GFP chromophore. *J Am Chem Soc*, 2012, 134: 1662–1672
- 84 Liu X Y, Chang X P, Xia S H, et al. Excited-state proton-transfer-induced trapping enhances the fluorescence emission of a locked GFP chromophore. *J Chem Theory Comput*, 2016, 12: 753–764
- 85 Xia S H, Cui G L, Fang W H, et al. How photoisomerization drives peptide folding and unfolding: Insights from QM/MM and MM dynamics simulations. *Angew Chem Int Ed*, 2016, 55: 2067–2072
- 86 Wu D, Wang Y T, Fang W H, et al. QM/MM studies on photoisomerization dynamics of azobenzene chromophore tethered to a DNA duplex: Local unpaired nucleobase plays a crucial role. *Chem Asian J*, 2018, 13: 780–784
- 87 Lan Z, Fabiano E, Thiel W. Photoinduced nonadiabatic dynamics of pyrimidine nucleobases: On-the-fly surface-hopping study with semiempirical methods. *J Phys Chem B*, 2009, 113: 3548–3555
- 88 Lan Z, Lu Y, Fabiano E, et al. QM/MM nonadiabatic decay dynamics of 9*H*-adenine in aqueous solution. *ChemPhysChem*, 2011, 12: 1989–1998
- 89 Barbatti M, Aquino A J A, Szymczak J J, et al. Relaxation mechanisms of UV-photoexcited DNA and RNA nucleobases. *Proc Natl Acad Sci USA*, 2010, 107: 21453–21458
- 90 Nachtigallova D, Zeleny T, Ruckebauer M, et al. Does stacking restrain the photodynamics of individual nucleobases? *J Am Chem Soc*, 2010, 132: 8261–8263
- 91 Lu Y, Lan Z, Thiel W. Hydrogen bonding regulates the monomeric nonradiative decay of adenine in DNA strands. *Angew Chem Int Ed*, 2011, 50: 6864–6867
- 92 Fazzi D, Barbatti M, Thiel W. Unveiling the role of hot charge-transfer states in molecular aggregates via nonadiabatic dynamics. *J Am Chem Soc*, 2016, 138: 4502–4511
- 93 Fischer S A, Lingerfelt D B, May J W, et al. Non-adiabatic molecular dynamics investigation of photoionization state formation and lifetime in Mn²⁺-doped ZnO quantum dots. *Phys Chem Chem Phys*, 2014, 16: 17507–17514
- 94 Nelson T, Fernandez-Alberti S, Roitberg A E, et al. Nonadiabatic excited-state molecular dynamics: Modeling photophysics in organic conjugated materials. *Acc Chem Res*, 2014, 47: 1155–1164
- 95 Gan Y, Yue L, Guo X, et al. Multi-state nonadiabatic deactivation mechanism of coumarin revealed by *ab initio* on-the-fly trajectory surface hopping dynamic simulation. *Phys Chem Chem Phys*, 2017, 19: 12094–12106
- 96 Guo X, Cao Z. Low-lying electronic states and their nonradiative deactivation of thieno[3,4-*b*]pyrazine: An *ab initio* study. *J Chem Phys*, 2012, 137: 224313
- 97 Gao X, Geng H, Peng Q, et al. Nonadiabatic molecular dynamics modeling of the intrachain charge transport in conjugated diketopyrrolo-pyrrole polymers. *J Phys Chem C*, 2014, 118: 6631–6640
- 98 Gao X, Peng Q, Niu Y, et al. Theoretical insight into the aggregation induced emission phenomena of diphenyldibenzofulvene: A nonadiabatic molecular dynamics study. *Phys Chem Chem Phys*, 2012, 14: 14207–14216
- 99 Xie W, Bai S, Zhu L, et al. Calculation of electron transfer rates using mixed quantum classical approaches: Nonadiabatic limit and beyond. *J Phys Chem A*, 2013, 117: 6196–6204

- 100 Chu W, Saidi W A, Zheng Q, et al. Ultrafast dynamics of photogenerated holes at a $\text{CH}_3\text{OH}/\text{TiO}_2$ rutile interface. *J Am Chem Soc*, 2016, 138: 13740–13749
- 101 Wang L, Long R, Prezhd O V. Time-domain *ab initio* modeling of photoinduced dynamics at nanoscale interfaces. *Annu Rev Phys Chem*, 2015, 66: 549–579
- 102 Wang L, Akimov A, Prezhd O V. Recent progress in surface hopping: 2011–2015. *J Phys Chem Lett*, 2016, 7: 2100–2112
- 103 Richter M, Marquetand P, González -Vázquez J, et al. SHARC: *Ab initio* molecular dynamics with surface hopping in the adiabatic representation including arbitrary couplings. *J Chem Theory Comput*, 2011, 7: 1253–1258
- 104 Habenicht B F, Prezhd O V. *Ab initio* time-domain study of the triplet state in a semiconducting carbon nanotube: Intersystem crossing, phosphorescence time, and line width. *J Am Chem Soc*, 2012, 134: 15648–15651
- 105 Granucci G, Persico M, Spighi G. Surface hopping trajectory simulations with spin-orbit and dynamical couplings. *J Chem Phys*, 2012, 137: 22a501
- 106 de Carvalho F F, Tavernelli I. Nonadiabatic dynamics with intersystem crossings: A time-dependent density functional theory implementation. *J Chem Phys*, 2015, 143: 224105
- 107 Curchod B F E, Rauer C, Marquetand P, et al. Communication: GAIMS-generalized *ab initio* multiple spawning for both internal conversion and intersystem crossing processes. *J Chem Phys*, 2016, 144: 101102
- 108 Fu B, Shepler B C, Bowman J M. Three-state trajectory surface hopping studies of the photodissociation dynamics of formaldehyde on *ab initio* potential energy surfaces. *J Am Chem Soc*, 2011, 133: 7957–7968
- 109 Bin L, Han K L. Mixed quantum-classical study of nonadiabatic dynamics in the $\text{O}(\text{}^3\text{P}_{2,1,0}, \text{}^1\text{D}_2) + \text{H}_2$ reaction. *J Phys Chem A*, 2009, 113: 10189–10195
- 110 Hu W, Lendvay G, Maiti B, et al. Trajectory surface hopping study of the $\text{O}(\text{}^3\text{P}) + \text{ethylene}$ reaction dynamics. *J Phys Chem A*, 2008, 112: 2093–2103
- 111 Takayanagi T. Quantum scattering calculations of the $\text{O}(\text{}^1\text{D}) + \text{N}_2(\text{X}^1\Sigma_g^+) \rightarrow \text{O}(\text{}^3\text{P}) + \text{N}_2(\text{X}^1\Sigma_g^+)$ spin-forbidden electronic quenching collision. *J Phys Chem A*, 2002, 106: 4914–4921
- 112 Pittner J, Lischka H, Barbatti M. Optimization of mixed quantum-classical dynamics: Time-derivative coupling terms and selected couplings. *Chem Phys*, 2009, 356: 147–152
- 113 Tapavicza E, Tavernelli I, Rothlisberger U. Trajectory surface hopping within linear response time-dependent density-functional theory. *Phys Rev Lett*, 2007, 98: 023001
- 114 Ryabinkin I G, Nagesh J, Izmaylov A F. Fast numerical evaluation of time-derivative nonadiabatic couplings for mixed quantum-classical methods. *J Phys Chem Lett*, 2015, 6: 4200–4203
- 115 Marian C M. Spin-orbit coupling and intersystem crossing in molecules. *WIREs Comput Mol Sci*, 2012, 2: 187–203
- 116 Wang F, Ziegler T, van Lenthe E, et al. The calculation of excitation energies based on the relativistic two-component zeroth-order regular approximation and time-dependent density-functional with full use of symmetry. *J Chem Phys*, 2005, 122: 204103
- 117 Wang F, Ziegler T. Theoretical study of the electronic spectra of square-planar platinum(II) complexes based on the two-component relativistic time-dependent density-functional theory. *J Chem Phys*, 2005, 123: 194102
- 118 van Lenthe E, Baerends E J, Snijders J G. Relativistic total-energy using regular approximations. *J Chem Phys*, 1994, 101: 9783–9792
- 119 van Lenthe E, van Leeuwen R, Baerends E J, et al. Relativistic regular two-component hamiltonians. *Int J Quantum Chem*, 1996, 57: 281–293
- 120 te Velde G, Bickelhaupt F M, Baerends E J, et al. Chemistry with ADF. *J Comput Chem*, 2001, 22: 931–967
- 121 Guerra C F, Snijders J G, te Velde G, et al. Towards an order-N DFT method. *Theor Chem Acc*, 1998, 99: 391–403
- 122 Baerends E J, Ziegler T, Atkins A J, et al. ADF2016, SCM, theoretical chemistry, Vrije Universiteit, Amsterdam, the Netherlands. <https://www.scm.com>
- 123 Vosko S H, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin-density calculations—A critical analysis. *Can J Phys*, 1980, 58: 1200
- 124 Becke A D. Density-functional exchange-energy approximation with correct asymptotic-behavior. *Phys Rev A*, 1988, 38: 3098–3100
- 125 Lee C T, Yang W T, Parr R G. Development of the colle-salvetti correlation-energy formula into a functional of the electron-density. *Phys Rev B*, 1988, 37: 785–789
- 126 Becke A D. A new mixing of hartree-fock and local density-functional theories. *J Chem Phys*, 1993, 98: 1372–1377
- 127 Hay P J, Wadt W R. *Ab initio* effective core potentials for molecular calculations—Potentials for K to Au including the outermost core orbitals. *J Chem Phys*, 1985, 82: 299–310
- 128 Harihara P C, Pople J A. Influence of polarization functions on molecular-orbital hydrogenation energies. *Theor Chim Acta*, 1973, 28: 213–222

- 129 Ditchfield R, Hehre W J, Pople J A. Self-consistent molecular-orbital methods. 9. Extended gaussian-type basis for molecular-orbital studies of organic molecules. *J Chem Phys*, 1971, 54: 724–728
- 130 Yanai T, Tew D P, Handy N C. A new hybrid exchange-correlation functional using the coulomb-attenuating method (CAM-B3LYP). *Chem Phys Lett*, 2004, 393: 51–57
- 131 Dunning T H. Gaussian-basis sets for use in correlated molecular calculations .1. The atoms boron through neon and hydrogen. *J Chem Phys*, 1989, 90: 1007–1023
- 132 Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 09, Revision A.02. Gaussian, Inc.: Wallingford, CT, 2009
- 133 Schulze M, Steffen A, Würthner F. Near-IR phosphorescent ruthenium(II) and iridium(III) perylene bisimide metal complexes. *Angew Chem Int Ed*, 2015, 54: 1570–1573
- 134 Jacquemin D, Escudero D. The short device lifetimes of blue PhOLEDs: Insights into the photostability of blue Ir(III) complexes. *Chem Sci*, 2017, 8: 7844–7850
- 135 You Y, Nam W. Photofunctional triplet excited states of cyclometalated Ir(III) complexes: Beyond electroluminescence. *Chem Soc Rev*, 2012, 41: 7061–7084
- 136 Liu Y, Sun X, Wang Y, et al. The influence of numbers and ligation positions of the triphenylamine unit on the photophysical and electroluminescent properties of homoleptic iridium(III) complexes: A theoretical perspective. *Dalton Trans*, 2014, 43: 11915–11924
- 137 Kleinschmidt M, van Wuelen C, Marian C M. Intersystem-crossing and phosphorescence rates in *fac*-Ir^{III}(ppy)₃: A theoretical study involving multi-reference configuration interaction wavefunctions. *J Chem Phys*, 2015, 142: 094301
- 138 Hay P J. Theoretical studies of the ground and excited electronic states in cyclometalated phenylpyridine Ir(III) complexes using density functional theory. *J Phys Chem A*, 2002, 106: 1634–1641
- 139 Pomarico E, Silatani M, Messina F, et al. Dual luminescence, interligand decay, and nonradiative electronic relaxation of cyclometalated iridium complexes in solution. *J Phys Chem C*, 2016, 120: 16459–16469
- 140 Zhang X, Jacquemin D, Peng Q, et al. General approach to compute phosphorescent OLED efficiency. *J Phy Chem C*, 2018, 122: 6340–6347
- 141 King K A, Spellane P J, Watts R J. Excited-state properties of a triply *ortho*-metalated iridium(III) complex. *J Am Chem Soc*, 1985, 107: 1431–1432
- 142 Sajoto T, Djurovich P I, Tamayo A B, et al. Temperature dependence of blue phosphorescent cyclometalated Ir(III) complexes. *J Am Chem Soc*, 2009, 131: 9813–9822
- 143 Tsuboyama A, Iwawaki H, Furugori M, et al. Homoleptic cyclometalated iridium complexes with highly efficient red phosphorescence and application to organic light-emitting diode. *J Am Chem Soc*, 2003, 125: 12971–12979
- 144 Chao H Y, Lu W, Li Y Q, et al. Organic triplet emissions of arylacetylide moieties harnessed through coordination to [Au(PCy₃)]⁺. Effect of molecular structure upon photoluminescent properties. *J Am Chem Soc*, 2002, 124: 14696–14706
- 145 Partyka D V, Esswein A J, Zeller M, et al. Gold(I) pyrenyls: Excited-state consequences of carbon-gold bond formation. *Organometallics*, 2007, 26: 3279–3282
- 146 Partyka D V, Teets T S, Zeller M, et al. Constrained digold(I) diaryls: Syntheses, crystal structures, and photophysics. *Chem Eur J*, 2012, 18: 2100–2112
- 147 Partyka D V, Zeller M, Hunter A D, et al. Relativistic functional groups: Aryl carbon-gold bond formation by selective transmetalation of boronic acids. *Angew Chem Int Ed*, 2006, 45: 8188–8191
- 148 Heng W Y, Hu J, Yip J H K. Attaching gold and platinum to the rim of pyrene: A synthetic and spectroscopic study. *Organometallics*, 2007, 26: 6760–6768
- 149 Vogt R A, Peay M A, Gray T G, et al. Excited-state dynamics of (organophosphine)gold(I) pyrenyl isomers. *J Phys Chem Lett*, 2010, 1: 1205–1211
- 150 Lima J C, Rodríguez L. Applications of gold(I) alkynyl systems: A growing field to explore. *Chem Soc Rev*, 2011, 40: 5442–5456
- 151 Lu W, Kwok W M, Ma C, et al. Organic triplet excited states of gold(I) complexes with oligo (*o*- or *m*-phenyleneethynylene) ligands: Conjunction of steady-state and time-resolved spectroscopic studies on exciton delocalization and emission pathways. *J Am Chem Soc*, 2011, 133: 14120–14135
- 152 Craig S, Gao L, Lee I, et al. Gold-containing indoles as anticancer agents that potentiate the cytotoxic effects of ionizing radiation. *J Med Chem*, 2012, 55: 2437–2451
- 153 Gao L, Niedzwiecki D S, Deligonul N, et al. Gold(I) styrylbenzene, distyrylbenzene, and distyrylnaphthalene complexes: High emission quantum yields at room temperature. *Chem Eur J*, 2012, 18: 6316–6327
- 154 Lu W, Chan K T, Wu S X, et al. Quest for an intermolecular Au(III)⋯Au(III) interaction between cyclometalated gold(III) cations. *Chem Sci*, 2012, 3: 752–755

- 155 Ma C, Chan C T L, Kwok W M, et al. Ligand π -conjugation dictated intersystem crossing in phenyleneethynylene gold(I) complexes. *Chem Sci*, 2012, 3: 1883–1892
- 156 Cui G L, Cao X Y, Fang W H, et al. Photoinduced gold(I)-gold(I) chemical bonding in dicyanoaurate oligomers. *Angew Chem Int Ed*, 2013, 52: 10281–10285
- 157 Iwamura M, Nozaki K, Takeuchi S, et al. Real-time observation of tight Au–Au bond formation and relevant coherent motion upon photoexcitation of $[\text{Au}(\text{CN})_2]^-$ oligomers. *J Am Chem Soc*, 2013, 135: 538–541
- 158 Latouche C, Lin Y R, Tobon Y, et al. Au–Au chemical bonding induced by UV irradiation of dinuclear gold(I) complexes: A computational study with experimental evidence. *Phys Chem Chem Phys*, 2014, 16: 25840–25845
- 159 Kim K H, Kim J G, Nozawa S, et al. Direct observation of bond formation in solution with femtosecond X-ray scattering. *Nature*, 2015, 518: 385–389
- 160 Vogt R A, Gray T G, Crespo-Hernández C E. Subpicosecond intersystem crossing in mono- and di(organophosphine)gold(I) naphthalene derivatives in solution. *J Am Chem Soc*, 2012, 134: 14808–14817
- 161 Iwamura M, Wakabayashi R, Maeba J, et al. Coherent vibration and ultrafast dynamics upon bond formation in excited dimers of an Au(I) complex. *Phys Chem Chem Phys*, 2016, 18: 5103–5107
- 162 Cui G L, Fang W H. State-specific heavy-atom effect on intersystem crossing processes in 2-thiothymine: A potential photodynamic therapy photosensitizer. *J Chem Phys*, 2013, 138: 044315

Summary for “过渡金属配合物非绝热动力学模拟的新进展”

Nonadiabatic dynamics simulation method for transition metal complexes: Theory, developments, and applications

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Excited-state related properties of transition metal complexes have received much attention in recent years due to their potential applications in the field of energy, material and biology. To fully understand the underlying mechanism, we always need to resort to ultrafast time-resolved spectroscopies as well as reliable *ab initio* nonadiabatic dynamics simulations. However, nonadiabatic dynamics simulation methods that are suitable for investigating excited-state dynamics of transition metal complexes still demand further developments to improve simulation efficiency and accuracy.

In this short review, we have shortly present some recent developments of non-adiabatic dynamics methods that are suitable for investigating excited state properties of transition metal complexes, mainly including Multi-Configuration Time Dependent Hartree (MCTDH) and mixed quantum-classical surface hopping methods. In addition, we have introduced our recently developed TD-DFT-based generalized trajectory surface hopping method in which an efficient algorithm of computing nonadiabatic couplings is realized. In combination with the classical path approximation, this newly developed method can effectively simulate internal conversion and intersystem crossing processes of transition metal complexes on an equal footing.

With this newly developed method, we have systematically investigated the early-time ultrafast excited-state dynamics of three Ir(III) complexes bearing distinct ligands. The ISC rates estimated by our simulations are 65, 81 and 140 fs, which agree quite well with experimentally measured ca. 80, 80 and 110 fs. These Ir(III) complexes show similar macroscopic phenomena, i.e., ultrafast IC and ISC, their microscopic excited-state relaxation dynamics are individually different, for example, electron and hole transfer dynamics. These new insights for excited-state dynamics of Ir(III) complexes could be helpful for rationally designing Ir-containing compounds with excellent photoluminescence performance.

In addition, we have also investigated the ultrafast intersystem crossing process of Au(I) naphthalene derivatives. We have found that (1) ultrafast and sub-picosecond intersystem crossing processes are mainly caused by small energy gaps and large spin-orbit couplings between S_1 and T_n . (2) Adding the second gold(I)-phosphine group does not increase spin-orbit couplings between S_1 and T_n but decrease their values remarkably, which implies that heavy-atom effects are state-specific, not-universal. (3) The position at which the second gold(I)-phosphine group is attached has remarkable influence on electronic structures of S_1 and T_n and their relative energies, which affect energy gaps and spin-orbit couplings between S_1 and T_n and eventually modulate intersystem crossing rates from S_1 to T_n . This work exemplifies that different isomers of a compound could have distinct excited-state relaxation dynamics.

Above simulation results not only agree pretty well with experiments, but also provide valuable insights into excited-state relaxation dynamics for these transition-metal-containing complexes. In one word, our present developments have established an efficient and accurate simulation tool for investigating excited-state dynamics of transition metal complexes.

transition metal complexes, nonadiabatic dynamics simulation, generalized trajectory surface hopping, internal conversion and intersystem crossing

doi: 10.1360/N972018-00897