Multichannel Quantum Defect Theory with a Frame Transformation for Ultracold Atom-Molecule Collisions in Magnetic Fields

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We extend the powerful formalism of multichannel quantum defect theory combined with a frame transformation to ultracold atom-molecule collisions in magnetic fields. By solving the coupled-channel equations with hyperfine and Zeeman interactions omitted at short range, the extended theory enables a drastically simplified description of the intricate quantum dynamics of ultracold molecular collisions in terms of a small number of short-range parameters. We apply the formalism to ultracold Mg + NH collisions in a magnetic field, achieving a 10^4-fold reduction in computational effort.

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Recent advances in cooling and trapping diatomic and polyatomic molecules have established ultracold molecular gases as an emerging platform for quantum information science, ultracold chemistry, and precision searches for new physics beyond the standard model [1–6]. The exquisite control over molecular degrees of freedom achieved in these experiments enables the exploration of novel regimes of ultracold chemical dynamics tunable by external electromagnetic fields [7–9]. However, the use of molecules for these applications has been hindered by rapid losses observed in ultracold molecular gases due to the formation of intermediate complexes in two-body collisions [10–17]. Therefore, understanding and controlling ultracold molecular collisions have long been recognized as major goals in the field [1–3]. This, however, has proven to be an elusive task due to the enormous number of molecular states (rotational, vibrational, fine, and hyperfine) strongly coupled by highly anisotropic interactions and external fields, which results in skyrocketing computational costs of rigorous coupled-channel (CC) calculations on ultracold molecular collisions [18,19]. While efficient basis sets have been developed to mitigate this problem [19–23], fully converged CC calculations including all degrees of freedom are yet to be reported on ultracold K + NaK [24,25], Na + NaLi [26,27], and Rb + KRb [16] collisions explored in recent experiments.

A promising avenue toward resolving these difficulties could be based on multichannel quantum defect theory (MQDT), an elegant technique for solving the time-independent Schrödinger equation based on the separation of distance and energy scales in ultracold collisions [28–39]. MQDT allows one to avoid the costly numerical procedure of solving CC equations over extended ranges of the radial coordinate R, collision energy, and magnetic field, leading to a substantial reduction of computational cost [35–42]. However, in conventional MQDT, it is still necessary to solve CC equations in the short-range collision complex region, which is forbiddingly difficult for the atom-molecule systems interacting via deep and strongly anisotropic potentials, such as those studied in recent experiments [16,24–27].

MQDT becomes especially powerful when combined with a frame transformation (FT) approach, in which the hyperfine-Zeeman structure of colliding atoms is neglected at short range. This results in a large reduction of computational effort and provides a physically meaningful description of ultracold atomic collisions in terms of a few short-range parameters [40–47]. An extension of MQDT-FT to the much more computationally intensive (and less well understood) ultracold molecular collisions would thus be highly desirable. Previous theoretical work has shown that MQDT can be successfully applied to describe ultracold atom-molecule collisions [35–38] and chemical reactions [39], but these calculations did not consider the essential FT aspect of MQDT, which makes it such an indispensable tool in modern ultracold atomic collision theory [40–46].

The application of MQDT-FT to atom-molecule collisions faces significant challenges due to uniquely complex features of molecular structure such as rotational states [48,49], multiple nuclear spins, and inherently anisotropic atom-molecule interactions [1–3].

Here, we show that the MQDT-FT approach can be extended to ultracold molecular collisions in a magnetic field, enabling one to drastically simplify their rigorous theoretical description. This is achieved by using compact CC basis sets at short range, which exclude the hyperfine and Zeeman interactions. These interactions are incorporated at long range via MQDT-FT boundary conditions, resulting in a complete description of ultracold atom-molecule collision dynamics across large collision energy and magnetic field ranges in terms of a small number of short-range parameters. These parameters can be used to, e.g., fit experimental observations and to obtain insight into complex molecular collision dynamics without performing expensive CC calculations. Our results show the potential of MQDT-FT to significantly extend the scope of ultracold atom-molecule collisions and chemical reactions amenable to rigorous quantum dynamical studies, which would facilitate the accurate characterization of atom-molecule Feshbach resonances observed in recent pioneering experiments [24–27], as well as new insights into quantum chaotic behavior and microscopic interactions in atom-molecule collision complexes [50].

Theory—We begin by briefly reviewing the key concepts of MQDT as they apply to ultracold atom-molecule collisions in a magnetic field. The Hamiltonian of the atom-molecule collision complex is (in atomic units) [51]

$$\hat{H} = -\frac{1}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{\mathbf{l}}^2}{2\mu R^2} + \hat{H}_{\rm as} + \hat{V}(R,\theta). \tag{1}$$

Below we will use ultracold $\mathrm{Mg}(^1\mathrm{S}) + \mathrm{NH}(\tilde{X}^3\Sigma^-)$ collisions as a representative example, which served as a test bed for applying MQDT to ultracold atom-molecule collisions [35]. In Eq. (1), μ and $\hat{\mathbf{l}}$ are the reduced mass and the orbital angular momentum for the collision, R is the atom-molecule distance, and $\hat{H}_{\rm as}$ is the asymptotic Hamiltonian

$$\hat{H}_{\rm as} = B_e\hat{\mathbf{N}}^2 + \hat{H}_{\rm fs} + \hat{H}_{\rm hfs} + \hat{H}_{\rm Z}, \tag{2}$$

where B_e is the rotational constant, $\hat{\mathbf{N}}$ is the rotational angular momentum of the molecule, $\hat{H}_{\rm fs} = \gamma_{\rm sr}\hat{\mathbf{N}}\cdot\hat{\mathbf{S}} + \frac{2}{3}\lambda_{\rm ss}\sqrt{(24\pi/5)}\sum_q(-1)^q Y_{2-q}(\hat{\boldsymbol{r}})[\hat{\mathbf{S}}\otimes\hat{\mathbf{S}}]^{(2)}_q$ is the intramolecular fine-structure Hamiltonian, which depends on the electron spin $\hat{\mathbf{S}}$ and the orientation of the molecular axis $\boldsymbol{r}$, and $\gamma_{\rm sr}$ and $\lambda_{\rm ss}$ are the spin-rotation and spin-spin interaction constants [52,53]. The Zeeman interaction $\hat{H}_{\rm Z} = g_S\mu_{\rm B}\mathbf{B}\cdot\hat{\mathbf{S}}$, where $g_S \simeq 2.002$ is the electron g factor, $\mu_{\rm B}$ is the Bohr magneton, the magnetic field vector $\mathbf{B}$ defines the space-fixed quantization axis z, and the hyperfine interaction $\hat{H}_{\rm hfs}$ is considered below. We use the *ab initio* interaction potential $V(R,\theta)$ for Mg + NH [54], which depends on R and the Jacobi angle θ [55].

In MQDT, the matrix solution $\boldsymbol{\Psi}$ of the Schrödinger equation $\hat{H}\boldsymbol{\Psi} = E\boldsymbol{\Psi}$ in the basis of eigenvectors of the asymptotic Hamiltonian [Eq. (2)] is matched to [33,35]

$$\boldsymbol{\Psi}(R_m) = R_m^{-1}[\boldsymbol{f}(R_m) + \boldsymbol{g}(R_m)\boldsymbol{K}^{\rm sr}], \tag{3}$$

where the matching radius $R = R_m$ marks the boundary between the short-range and long-range regions, E is the total energy, $\boldsymbol{K}^{\rm sr}$ is the short-range K matrix, which includes open and weakly closed channels, and $\boldsymbol{f}(R)$ and $\boldsymbol{g}(R)$ are diagonal matrices of regular and irregular reference functions [55]. The transition T matrix and state-to-state integral cross sections are obtained from $\boldsymbol{K}^{\rm sr}$ following the standard sequence of MQDT steps, which involves taking into account the coupling between the open and weakly closed channels, and the threshold effects [55]. Because the $N_{\rm ref}$ reference channels are decoupled at $R \geq R_m$, this procedure is computationally efficient, scaling linearly with $N_{\rm ref}$.

In the spirit of MQDT-FT for atomic collisions [40–46], we seek to describe short-range quantum dynamics with a simplified Hamiltonian $\hat{H}_0$ obtained by omitting the terms, which are small compared to $\hat{V}$, from $\hat{H}_{\rm as}$ in Eq. (2). We then solve the Schrödinger equation $\hat{H}_0\boldsymbol{\Psi}_0 = E\boldsymbol{\Psi}_0$ subject to the boundary conditions [33,35]

$$\boldsymbol{\Psi}_0(R_m) = R_m^{-1}[\boldsymbol{f}(R_m) + \boldsymbol{g}(R_m)\boldsymbol{K}^{\rm sr}_0] \tag{4}$$

to obtain $\boldsymbol{K}^{\rm sr}_0$, the MQDT-FT analog of the short-range K matrix. Note that $\hat{H}_0$ only occurs in MQDT-FT, but not in conventional MQDT. In atomic MQDT-FT, $\hat{H}_0$ is typically chosen by omitting the hyperfine and Zeeman interactions of the collision partners from $\hat{H}$ [40–46]. By contrast, as shown below, in atom-molecule MQDT-FT it is possible to choose $\hat{H}_0$ in several nonequivalent ways depending on the nature of the collisional transition of interest, demonstrating the flexibility of the technique.

The exact short-range K matrix ($\boldsymbol{K}^{\rm sr}$) defined by Eq. (3) is then approximated as

$$\boldsymbol{K}^{\rm sr} \simeq \boldsymbol{U}^{\dagger}\boldsymbol{K}^{\rm sr}_0\boldsymbol{U}, \tag{5}$$

where $\boldsymbol{U}$ is an orthogonal matrix composed of the eigenvectors of the asymptotic Hamiltonian [Eq. (2)] [55]. Note that $\boldsymbol{K}^{\rm sr}_0$ is much easier to compute than $\boldsymbol{K}^{\rm sr}$ because $\hat{H}_0$ can be chosen in such a way as to exclude the small hyperfine and Zeeman interactions [57], thus eliminating the need to use enormous CC basis sets including the electron and/or nuclear spin basis functions of the collision partners [23]. In addition, since $\hat{H}_0$ is independent of external fields, $\boldsymbol{K}^{\rm sr}_0$ can be efficiently computed using the total angular momentum (TAM) basis as shown below, and it is independent of M, the z projection of J.

Results—We now apply MQDT-FT to describe the quantum dynamics of ultracold Mg + NH collisions in a magnetic field, focusing on the inelastic transitions between the different Zeeman sublevels of $\mathrm{NH}(N = 0)$ labeled by the z-projection of the molecule's electron spin $M_S = -1$, 0, 1. These transitions cause trap loss and thus limit the efficiency of sympathetic cooling of NH molecules by Mg atoms [52]. For now, we neglect the hyperfine interaction ($\hat{H}_{\rm as} = B_e\hat{\mathbf{N}}^2 + \hat{H}_{\rm fs} + \hat{H}_{\rm Z}$) and choose the simplified short-range Hamiltonian $\hat{H}_0$ by neglecting the Zeeman interaction as $\hat{H}_0 = \hat{H} - \hat{H}_{\rm Z}$. Since $\hat{H}_0$ is field-independent, we obtain $\boldsymbol{K}^{\rm sr}_0$ by solving CC equations in the

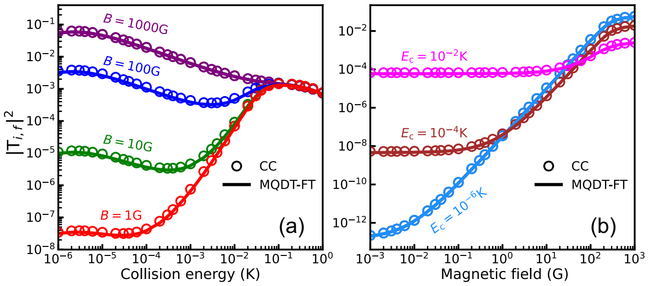

FIG. 1. Probabilities for the spin relaxation transition $M_S = 1(l = 0) \rightarrow M'_S = 0(l' = 2)$ in cold $\mathrm{Mg} + {}^{14}\mathrm{NH}(N = 0)$ collisions plotted as a function of collision energy (a) and magnetic field (b). Solid lines—MQDT-FT calculations, open circles—exact CC results.

TAM basis $|(NS)jlJM\rangle$, where $\hat{\mathbf{J}} = \hat{\mathbf{l}} + \hat{\mathbf{j}}$ is the total angular momentum of the atom-molecule system and $\hat{\mathbf{j}} = \hat{\mathbf{N}} + \hat{\mathbf{S}}$ is that of the diatomic molecule. Because $\hat{H}_0$ is block diagonal in J and independent of M, the computational cost of MQDT-FT is much smaller than that of conventional MQDT [35].

Figure 1 compares the probabilities $|T_{i\rightarrow f}|^2$ for the spin relaxation transition $M_S = 1 \rightarrow 0$ between the Zeeman levels of NH $(N = 0)$ in cold $\mathrm{Mg} + \mathrm{NH}$ collisions calculated using MQDT-FT with exact CC results. Encouragingly, MQDT-FT provides an essentially exact description of the transition probability as a function of collision energy *and* external magnetic field with only 139 channels as compared to 954 channels required in standard MQDT [36], a ≃7-fold reduction in the number of channels. Because the computational cost of solving CC equations scales as N^3 with the number of channels N, MQDT-FT offers a ≃320-fold increase in computational efficiency over standard MQDT.

The excellent performance of MQDT-FT illustrated in Fig. 1 validates the assumption that $\hat{H}_Z$ plays a negligible role in short-range dynamics. The strong magnetic field dependence of the inelastic probability at 1 μK thus arises entirely from long-range physics. Specifically, inelastic scattering is suppressed by the centrifugal barrier in the outgoing d-wave channel at low magnetic fields [58,59]. This is an example of physically meaningful insight into ultracold atom-molecule collisions gained from MQDT-FT simulations.

We next address the question of whether MQDT-FT can be used to describe hyperfine interactions, which play a crucial role in ultracold molecular collisions [2,17], yet are notoriously difficult to describe using standard CC methods, requiring enormous basis sets [23]. As depicted in Fig. 2(a) the hyperfine structure of ^{15}NH arises from the nuclear spins of ^{15}N $(I_1 = 1/2)$ and H $(I_2 = 1/2)$, which couple to $\hat{\mathbf{j}}$ (see above) to produce the total angular momentum $\hat{\mathbf{F}}$ of NH, which is a good quantum number at low B field. The hyperfine structure is described by the Hamiltonian $\hat{H}_{\mathrm{hf}} = \sum_{i=1,2} a_i \hat{\mathbf{I}}_i \cdot \hat{\mathbf{S}} + \hat{H}_{\mathrm{ahf}}$, where $\hat{H}_{\mathrm{ahf}} = \sum_{i=1,2}(c_i\sqrt{6}/3)\sqrt{(4\pi/5)}\sum_q(-1)^q Y_{2-q}(\boldsymbol{r})[\hat{\mathbf{I}}_i \otimes \hat{\mathbf{S}}]^{(2)}_q$ is the anisotropic hyperfine interaction, and a_i and c_i are the isotropic and anisotropic hyperfine constants for the ith nucleus [55,60,61]. In the high B-field limit, the 12 hyperfine levels of ^{15}NH are arranged in three groups, with four states per group, according to the value of $M_S = -1$, 0, and 1, as shown in Fig. 2(b).

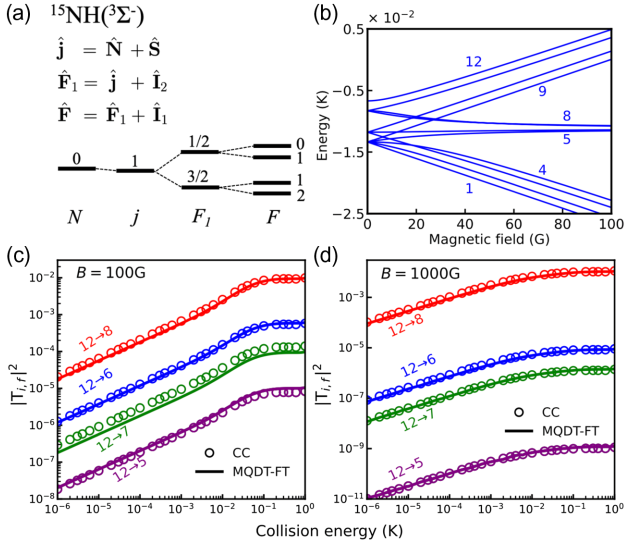

FIG. 2. Hyperfine energy levels of ^{15}NH $(N = 0)$ at zero field (a) and as a function of magnetic field (b). State-to-state transition probabilities $|T_{il,fl'}|^2$ plotted as a function of collision energy at $B = 100$ G (c) and $B = 1000$ G (d) for $\mathrm{Mg} + \mathrm{NH}(N = 0)$ collisions for $l = 0$ and $l' = 2$. Solid lines—MQDT-FT calculations, open circles—exact CC results. The initial and final states of NH are indicated next to each curve as $i \rightarrow f$ [see panel (b)].

To account for the hyperfine structure, we perform MQDT-FT calculations using the same simplified short-range Hamiltonian $\hat{H}_0$ and the TAM basis set as described above without extra computational costs. It is only necessary to augment $\boldsymbol{K}_0^{\mathrm{sr}}$ by the nuclear spin basis states $|I_1 M_{I_1}\rangle|I_2 M_{I_2}\rangle$ before applying the FT [55].

Figures 2(c) and 2(d) show transition probabilities between the different hyperfine levels of NH in ultracold collisions with Mg atoms. We observe very good agreement between MQDT-FT and exact CC results, which indicates that the effects of hyperfine structure on ultracold atom-molecule collisions can be accurately described by MQDT-FT. Importantly, only 147 channels need to be coupled in our MQDT-FT calculations, whereas full CC computations involve as many as 3854 channels [53]. Thus, MQDT-FT affords a massive reduction of computational cost by the factor of $(3854/147)^3 \simeq 1.8 \times 10^4$.

An attractive feature of the MQDT-FT approach is its capability to describe the complex quantum dynamics of ultracold collisions in terms of a small number of

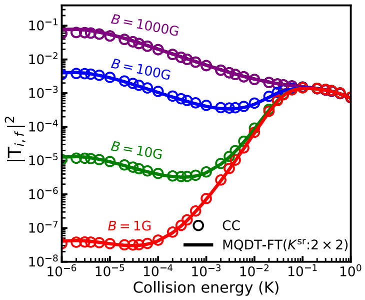

FIG. 3. Probabilities for the transition $M_S = 1(l = 0) \rightarrow M'_S = 0(l' = 2)$ in cold Mg + ^{14}NH($N = 0$) collisions as a function of collision energy. Solid lines—MQDT-FT calculations based on a 2×2 short-range K-matrix ($K^{\mathrm{sr}}: 2 \times 2$), open circles—exact CC results.

"universal" parameters [41,42]. While this capability has provided invaluable physical insight into ultracold atomic collisions [41,42], it has been unclear whether it can be extended to more complex molecular collisions. A minimal MQDT-FT model of ultracold Mg + NH collisions is based on a 2×2 short-range K matrix obtained using only the elements of $\boldsymbol{K}^{\mathrm{sr}}$ corresponding to the initial and final channels (K^{sr}_{ii}, $K^{\mathrm{sr}}_{if} = K^{\mathrm{sr}}_{fi}$, and K^{sr}_{ff}).

As shown in Fig. 3, the probability for the $M_S = 1 \rightarrow M'_S = 0$ transition obtained with the two-channel model is in excellent agreement with the full 954-channel results. Remarkably, the quantum dynamics of inelastic spin relaxation in ultracold Mg + NH collisions in a magnetic field can be described nearly exactly using just three short-range parameters (K^{sr}_{ii}, K^{sr}_{if}, and K^{sr}_{ff}) over a wide range of collision energies. This result highlights the universal nature of complex ultracold atom-molecule collisions in a dc magnetic field, and suggests MQDT-FT as a possible alternative to the approaches based on a single-channel universal model [62,63]. While the phenomenological y parameter of the universal model can be related to the results of CC calculations only in some special cases [63], the MQDT-FT parameters (K^{sr}_{ij}) are readily available from modest CC calculations, which only need to be performed in the short-range region, and do not need to include the Zeeman and hyperfine interactions.

We next consider the possibility of MQDT-FT based on an even more drastically simplified short-range Hamiltonian $\hat{H}_0$, *which includes only rovibrational degrees of freedom*. The flexibility in choosing $\hat{H}_0$ is an essential new aspect of atom-molecule MQDT-FT as opposed to atomic MQDT-FT [40–46]. Because of the absence of all spin-dependent interactions in $\hat{H}_0$, it cannot describe inelastic transitions between the different hyperfine-Zeeman sublevels of NH($N = 0$), which, for collisions with structureless atoms such as Mg, are mediated by intramolecular spin-dependent interactions [51,59]. We thus focus on inelastic transitions between the different fine-structure components of excited rotational states of NH.

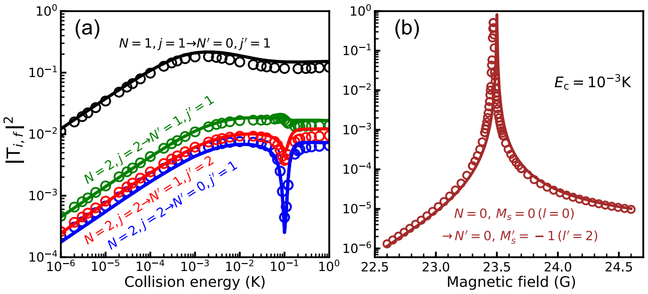

FIG. 4. (a) Collision energy dependence of transition probabilities between the different fine-structure levels of ^{14}NH in ultracold collisions with Mg atoms. Solid lines—MQDT-FT calculations, open circles—exact CC results obtained using the recoupling FT. All results are for a single incident s-wave component ($l = 0$) and summed over all final l'. (b) Magnetic field dependence of the spin relaxation probability in cold Mg + ^{14}NH($N = 0$) collisions. Solid line—MQDT-FT calculations, open circles—exact CC results. The quantum numbers for the initial and final states involved in each transition are indicated next to the corresponding curves.

We obtain $\boldsymbol{K}^{\mathrm{sr}}_0$ by solving CC equations in the basis set $|(Nl)J_r M_r\rangle$, where $\hat{\mathbf{J}}_r = \hat{\mathbf{N}} + \hat{\mathbf{l}}$ is the total rotational angular momentum of the collision complex [23]. The basis functions $|(Nl)J_r M_r\rangle$ are the eigenstates of $\hat{H}_{0,\mathrm{as}}$, the asymptotic Hamiltonian part of $\hat{H}_0$. The eigenstates of $\hat{H}_{\mathrm{as}} = \hat{H}_{0,\mathrm{as}} + \hat{H}_{\mathrm{fs}}$ are well approximated by the TAM basis functions $|(NS)jlJM\rangle$ for $^{2S+1}\Sigma$ molecules [64] provided the weak spin-spin interaction between the different N states can be neglected. Our FT employs an analytical recoupling formula between the total rotational angular momentum and TAM bases (see Eq. (2.27) of Ref. [64] and the Supplemental Material [55]), which has been successfully applied to calculate the T matrix for atom-molecule collisions above 5 K [64–68].

Figure 4(a) shows that the probabilities for rotationally inelastic fine-structure transitions in ultracold Mg + NH collisions are well described by MQDT-FT. Thus, using a spin-independent $\hat{H}_0$ in short-range CC calculations in the framework of MQDT-FT enables one to describe a wide range of transitions between rotational and fine-structure levels of open-shell molecules in ultracold collisions with atoms.

We finally subject our MQDT-FT approach to a stringent test by exploring its ability to reproduce magnetic Feshbach resonances in atom-molecule collisions, whose positions and widths are highly sensitive to fine details of short-range atom-molecule interactions [69]. In Fig. 4(b) we show the magnetic field dependence of the spin-relaxation probability in cold Mg + ^{14}NH($N = 0$) collisions, which displays a pronounced Feshbach resonance due to closed-channel states in the $N = 0$ and $N = 1$ manifolds coupled to the incident channel by the short-range anisotropic Mg-NH interaction. We observe excellent agreement between MQDT-FT calculations and exact CC results, demonstrating that the MQDT-FT approach is capable of predicting the properties of magnetic Feshbach resonances. The error in the resonance position does not exceed 0.1%, comparable to the performance of MQDT-FT for ultracold $\mathrm{Rb} + \mathrm{Rb}$ collisions [40].

In summary, we have generalized the powerful MQDT-FT approach to ultracold atom-molecule collisions in external magnetic fields, providing a robust conceptual and numerical framework for their theoretical description. We have applied the approach to a realistic atom-molecule collision system ($\mathrm{Mg} + \mathrm{NH}$) using a variety of short-range Hamiltonians, obtaining encouraging agreement with exact CC calculations in all cases. Our calculations show that MQDT-FT can provide a dramatic (10^4-fold) reduction of computational effort of CC calculations of atom-molecule collisions compared to standard MQDT [36]. In many cases of practical interest, it will only be necessary to solve CC equations in the strong interaction region employing a rovibrational (TAM) basis in the absence of external fields, which can be accomplished using currently available computational techniques [38,50,70–73]. This opens up the possibility of performing rigorous quantum scattering calculations on a wide array of previously intractable ultracold atom-molecule collisions and chemical reactions in external fields, including those probed in recent experiments [16,24–27].

From a conceptual viewpoint, our results show that it is possible to describe the intricate quantum dynamics of ultracold atom-molecule collisions over wide ranges of collision energies and magnetic fields in terms of a small number of short-range parameters (three for $\mathrm{Mg} + \mathrm{NH}$). This provides a solid basis for the development of few-parameter MQDT-FT models of ultracold atom-molecule (and possibly even molecule-molecule [74]) collisions.

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