Laser-coolable polyatomic molecules with heavy nuclei

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Received 3 July 2017, revised 18 September 2017
Accepted for publication 26 September 2017
Published 30 October 2017

Abstract
Recently, a few diatomic and polyatomic molecules have been identified as prospective systems for Doppler/Sisyphus cooling. Doppler/Sisyphus cooling allows us to decrease the kinetic energy of molecules down to μK temperatures with high efficiency and allows their capture in molecular traps, including magneto-optical traps. Trapped molecules can be used for creating molecular fountains and/or performing controlled chemical reactions, high-precision spectra measurements, and a wealth of other applications. Polyatomic molecules with heavy nuclei are of considerable interest for the ‘new physics’ search outside of the Standard Model and other applications including cold chemistry and photochemistry, quantum informatics, etc. Here, we focus on the radium monohydroxide molecule (RaOH), which is on the one hand amenable to laser cooling and on the other hand opens excellent possibilities for P-odd and T-odd effects research. At present, RaOH is the heaviest polyatomic molecule proposed for direct cooling with lasers.

Supplementary material for this article is available online

Keywords: laser cooling, parity violation, transition moments, electronic structure, spin–orbit interaction

( Some figures may appear in colour only in the online journal)

Introduction

The scheme of molecular Doppler cooling (first displayed in [1]) has proved to be efficient, robust and applicable to a large class of molecular species. Recently, highly-efficient cooling and magneto-optical trapping of diatomic molecules has been demonstrated for SrF [2], YO [3] and CaF [4, 5]. The experiments on Doppler/Sisyphus cooling on BaH [6], MgF [7] and some other molecules and positive molecular ions are currently being conducted by different groups. Recently, we proposed a number of polyatomic molecules containing light atoms, which could possibly be suitable for Doppler/Sisyphus cooling [8]. The estimate for Doppler limit temperature for the considered molecules (CaOH, CaNC, MgCH3, CaCH3 and chiral MgCHDT) showed that it is possibly realistic to reach sub-mK temperatures with a large class of polyatomic species (see also recent proposal by Kozyryev et al [9] for a number of polyatomic radicals amenable to laser cooling). In 2017, J Doyle’s team at Harvard University reported the first observation of fast Sisyphus laser cooling of SrOH to the temperature of ~750 μK [10]. To the best of our knowledge, the only rival method currently allowing the cooling of polyatomic molecules (including more than three atoms) to sub-mK temperatures is the optoelectrical Sisyphus cooling method [11, 12]. The latter method, though having great potential, relies on strong Stark interaction with an external field and is expected to be particularly efficient when applied to molecules with rather large dipole moments. In contrast, the method of molecular laser cooling can be applied to dipolar and non-dipolar species with equal success. Furthermore, it is directly related to the well-studied, efficient and robust atomic Doppler cooling technique. Molecules of heavy element compounds are of particular interest for ultra-low temperature physics. On the one hand, electronic structures of...
heavy-atom molecules favor quasi-diagonality of Franck-Condon (FC) matrices between ground and excited electronic states [13] due to more diffuse valence electronic orbital in comparison with light-atom homologies. On the other hand, the molecular species containing heavy atoms are of considerable interest for the experiments devoted to searching for physics beyond the Standard Model [14–16], including searching for axion-like-particle candidates for dark matter [17] and parity violation in chiral molecules (see e.g. [18]).

In this work, we apply the principles for identifying the laser-coolable polyatomic species introduced in [8] to the field of heavy-atom compounds, and propose the triatomic molecule RaOH as a candidate for both Doppler cooling and detection of space parity violation (P-odd effects). It could also be used for the detection of both space parity and time-reversal violating (P, T-odd) interactions with polyatomic molecules. In the first part of the article, we calculate molecular spectroscopic parameters for the first excited and ground electronic states of RaOH, and estimate the completeness of the cooling loop by calculating the FC matrix for vibronic transitions between these states. We then apply the recently developed original methodology to compute transition electric dipole moments between these states within a fully-relativistic framework. Finally, we use the approach (developed by us earlier) to estimate P-odd and P, T-odd parameters of effective molecular spin Hamiltonian within the zeroth-order regular approximation (ZORA) [19, 20] (see also [21, 22]).

Relativistic electronic structure calculations

Equilibrium molecular parameters

As has been pointed out in [13], the crucial prerequisite for the closed cooling transition loop in molecules (required for the quasi-diagonality of the FC matrix) is the similarity of the equilibrium molecular geometries for the ground and first excited electronic states. This requirement is usually satisfied when the transition between these states is dominated by a transfer of a valence electron between non-bonding orbitals. In [8], we proposed a simple scheme for constructing the molecular structures of polyatomic species, which contain non-bonding single-occupied molecular orbitals. The basic idea is to substitute the halogen in the series of MX molecules (M is the metal and X is the halogen) to pseudo-halogen or functional groups. In our consideration in [8], the heaviest nucleus in a molecule was calcium (with the charge number Z = 20). Thus, we were able to safely neglect the relativistic effects in electronic structure calculations. For light element compounds, such an approximation indeed does not lead to noticeable changes in molecular parameters (see e.g. [23]).

In contrast, for heavy element compounds one has to account for relativistic effects on FC factors. FC factors are known to be strongly dependent on displacements in equilibrium geometries and can be sensitive to both scalar and spin-dependent relativistic effects, if such effects are different for the considered electronic states (in our case, the ground and first excited electronic states).

There are several methods of electronic structure calculations taking into account the relativistic effects at different levels of accuracy. Accounting for scalar-relativistic effects is a rather simple task, which can be performed with moderate computational effort using the spin-averaged relativistic effective core potential (ARECP) approximation (see e.g. [24, 25]). However, the effects of spin-dependent relativistic interactions and therefore the errors of scalar-relativistic calculations, especially for open-shell electronic states of molecules of heavy element compounds, are by no means negligible. Therefore, one has to invoke the methods properly accounting for the spin-dependent effects; unfortunately, these methods are much more sophisticated and computationally demanding than their scalar-relativistic counterparts. A good accuracy/cost ratio is achieved by the methods of this group based on the use of four-component spinors and many-electron Dirac–Coulomb Hamiltonian combined with the correlation treatment by the coupled cluster technique; we have used such a method for potential surface and transition dipole calculations. Note that for a wide spectrum of purposes, the computations can be partially simplified by approximate transformation to two-component spinors (i.e. quasirelativistic techniques) with no significant loss of precision. For a comprehensive review of relativistic techniques of electronic structure modeling see, e.g. [23].

We started our study with the calculation of equilibrium structures and normal modes for both ground and first excited electronic states of RaOH using ARECP with ten valence electrons treated explicitly for Ra and with all-electron description for O and H. The multiconfiguration self-consistent field method (MCSCF) is used for ARECP calculations with 17 valence electrons correlated and with the basis sets of triple-zeta quality taken from the MOLPRO program package library (see Supplementary material is available online at stacks.iop.org/JPB/50/225101/mmedia for details). The resulting equilibrium structures and normal mode frequencies are shown in table 1. It can be seen that RaOH has essentially linear geometry in both ground (2Σ+, according to irreps of C_{av} group) and first excited (2Π) electronic states. A very weak Renner–Teller effect in the 2Π state of RaOH detected within the spin–orbit-free approximation is consistent with the smallness of similar effects in light homolog compound CaOH [26, 27] and should be fully suppressed due to strong spin–orbit interaction in heavy-atom compounds. We emphasize that the vibrational analysis was not restricted to totally symmetric modes. To estimate the influence of the relativistic spin-dependent interaction on relative displacements in equilibrium geometries, we computed the properties for the states of interest with the scalar-relativistic four-component spin-free (SF) [28] and fully-relativistic four-component Dirac–Coulomb (DC) Hamiltonians. In the four-component calculations, we used the Fock-space relativistic coupled cluster with single and double excitations (FS-CCSD) method to account for electron correlations [29]. In this approach, the augmented basis set of atomic natural orbitals (ANO) optimised for RCC calculations (ANO-RCC) on Ra and double zeta plus polarization quality basis sets by Ahlrichs et al. on O and H (see Supplementary
Table 1. Calculated molecular parameters and FC factors for the RaOH molecule. The results of ARECP/MCSCF, SF/FS-RCCSD and DC/FS-RCCSD calculations are provided. Internuclear distances \( R_i \) are given in Å, electric dipole moments in Debye, transition wavenumbers \( T_e \) and harmonic vibrational wavenumbers \( \tilde{\omega}_n \) of normal mode \( \nu_l \) in \( \text{cm}^{-1} \). For FC factors, the corresponding vibrational quantum numbers are reported, e.g. \( \nu_{12}^0 \) is the FC factor for a vibronic transition between the ground (0) vibrational state of the excited electronic state and the vibrational state with the first mode (1) (Ra–O stretching) being doubly excited (2) in the ground electronic state.

| State \(( \Sigma )\) | ARECP/MCSCF | SF/FS-RCCSD | DC/FS-RCCSD |
|-----------------|------------|-------------|-------------|
| \( R_{\text{Ra–O}} \) | 2.38       | 2.30        | 2.30        |
| \( R_{\text{O–H}} \) | 0.94       | 0.94        | 0.94        |
| \( \angle \text{Ra–O–H} \) | 180.0      | 180.0       | 180.0       |
| \( |D| \) | 2.09       | 1.70        | 1.70        |
| \( T_e \) | 12.0 \( \times 10^3 \) | 13.8 \( \times 10^3 \) | 12.6 \( \times 10^3 \) |

Normal modes \( \nu_l \)

| \( \nu_1(\sigma^+ \) | 4243 | 4248 |
| \( \nu_2(\pi \) | 366  | 383  |

FC factors

\( \nu_{12}^0 \) \( \nu_{11}^1 \) \( \nu_{12}^2 \)

\( \sum > 0.99 \)

Figure 1. Potential energies of the ground and first excited electronic state as functions of \( R_{\text{Ra–O}} \) (left) and the valence Ra–O–H angle (right) with other parameters fixed at their equilibrium values (see supplementary material for details). All energies are given with respect to the ground state equilibrium energy. Solid black lines: DC/FS-RCCSD, dashed blue lines: SF/FS-RCCSD.
material) were used. Thus, we could also directly check the robustness of the calculated FC factors to changing the method for electron correlation accounting. The results of ARECP/MCSCF calculations indicate that the vibrations localized on the Ra–OH bond are of primary interest. Thus, one has to consider the cross-sections of the potential energy surfaces along the Ra–OH bond (while the relative positions of O and H nuclei can be fixed) first. The equilibrium Ra–O–H bond angle is expected to be very close to 180° due to the above-mentioned suppression of Renner–Teller effect by spin–orbit interaction. In order to re-confirm this, we explicitly calculated the dependence of the energies of the ground and first excited electronic states on the Ra–O–H bond angle (see figure 1) within the framework of the DC/FS-RCCSD approach. One can see from table 1 that the relative positions of the equilibrium points of the ground and excited electronic states of RaOH are nearly independent of the method used for accounting for electronic correlations as well as of the incorporation or exclusion of spin–orbit interactions. In contrast, the exclusion of spin-dependent relativistic interactions in the SF/FS-RCCSD leads to significant overestimation of computed excitation energies. This is natural, since the SF/FS-RCCSD approximation provides an estimate for the averaged energy of several individual electronic states differing essentially in the coupling of the spin and spatial angular momenta (spin–orbit multiplet), and the A state is the lowest state of this manifold. To directly check the influence of dynamic electronic correlations and the spin–orbit interaction on FC factors, we have calculated these factors for 0′ – 0, 0′ – 1 and 0′ – 2 transitions of the quasimolecule RaX. Here 0′, 0, 1 and 2 are the vibrational quantum numbers of the first excited electronic state (with prime) and ground electronic state (without prime), respectively; the mass of quasimolecule X is equal to that of the OH group (17 a.m.u.), while the internuclear potential is equivalent to that between Ra and O nuclei from either ARECP/MCSCF or SF/FS-RCCSD or DC/FS-RCCSD calculations (see Supplementary material). The calculations of FC factors were carried out analogously to those in [13] and the results are presented in table 1 and in the Supplementary material. Similar to [8], we are using here the sum of the three largest FC factors in order to estimate the completeness of the cooling loop. One can see from table 1 that for every calculation the sum of the three largest FC factors is greater than 0.99. Thus, it is reasonable to expect highly-closed cooling transition 5Σ1/2 → 2Π1/2 in RaOH.

Transition dipole moments

Another prerequisite for the efficient molecular Doppler cooling is strongly allowed dipole transition between working electronic states. To estimate radiative lifetimes for the first excited 3Π1/2 state on the FS-RCCSD level, we evaluated the transition electric dipole moment (TDM) between this state and the ground 5Σ1/2 electronic state using the finite-field method. The TDM component values were derived from the finite-difference approximation for the derivative matrix elements as

\[
TDM_{\eta} = \left( E_{\Pi_{1/2}} - E_{\Sigma_{1/2}} \right) \left( \frac{\partial \Psi_{\Pi_{1/2}}(F_\eta)}{\partial F_\eta} \frac{\partial \Psi_{\Sigma_{1/2}}(F_\eta)}{\partial F_\eta} \right)_{F_\eta = 0} \\
\approx \left( E_{\Pi_{1/2}} - E_{\Sigma_{1/2}} \right) \frac{\left( \Psi_{\Pi_{1/2}}^\dagger \frac{\partial \Psi_{\Pi_{1/2}}}{\partial F_\eta} \Psi_{\Sigma_{1/2}} \right)}{2\Delta F_\eta},
\]

(1)

Here, F is the applied uniform electric field strength, and $\Psi_{\Pi_{1/2}}$ and $\Psi_{\Sigma_{1/2}}$ stand for left and right eigenvectors of the field-dependent non-Hermitian FS-RCC effective Hamiltonian acting in the field-free (F = 0) model space. The numerical differentiation step size used, $\Delta F_\eta = 5 \cdot 10^{-5}$ atomic units, approximately corresponds to the center of the interval on the logarithmic scale in which the dependence of the resulting TDM values on the step size was negligible. Although the calculations involve only the effective Hamiltonian eigenvectors, i.e. the model space projections of many-electron wavefunctions, the resulting transition moment approximations implicitly incorporate the bulk of the contributions from the remaining (outer-space) part of these wavefunctions [30]. The computational procedure has been implemented within the DIRAC15 program package [31]. The lifetimes of several vibrational levels $v'$ are estimated as

\[
\tau_{v'} = \frac{4.936 \cdot 10^5}{|TDM|^2 \sum (FC)_{v'v'} \Delta E_{v'}^3},
\]

(2)

[32], where $\tau_{v'}$ is the radiative lifetime of the upper state vibrational level $v'$ (in s); |TDM|$^2$ is the sum of the squares of transition dipole moment moduli between one component of the initial electronic state and both components of the final state (in atomic units); (FC)$_{v'v'}$ is the FC factor for the vibronic transition $v'v'$, and $\Delta E$ is the energy interval between the vibronic levels $v'v'$ (in wavenumbers). The TDM value is evaluated at the equilibrium geometry of the ground electronic state of RaOH (which nearly coincides with that of the excited state) from DC/FS-RCCSD calculations. For $v' = 0$, we obtain the lifetime of the excited electronic state $\tau_0 \approx 40$ ns. Estimating the Doppler limit temperature $T_D$ as

\[
T_D = h/\left( 2k_B \tau_0 \right)
\]

[33], where $k_B$ is the Boltzman constant and $\hbar = \hbar/(2\pi)$ is the reduced Planck constant, results in $T_D \approx 90 \mu K$.

We have also calculated the dependence of the TDM on the internuclear distance Ra–O near the equilibrium to control possible Herzberg–Teller contribution to the vibrational spectrum (see figure 2). This contribution is proportional to the TDM derivative with respect to the internuclear distance Ra–O. To demonstrate the influence of the spin-dependent effects, we plot TDMs from DC/FS-RCCSD calculations along with the spin–orbit-free limit of the total TDM from SF/FS-RCCSD calculations and the longitudinal component $|M_z|$, which vanishes at the scalar-relativistic limit. Rather slow and nearly linear variation of the TDM near the equilibrium geometries of the ground and first excited electronic
moment, are reliably reproduced within the ZORA framework [38]. High-precision FS-RCC calculations of $P$-odd and $\mathcal{P}$, $T$-odd molecular parameters for the RaF molecule [39] are also in a good agreement with our previous estimates of electronic correlation effects on $P$-odd and $\mathcal{P}$, $T$-odd parameters.

Here, we briefly outline the fully-relativistic (four-component) operators describing nuclear spin-dependent $P$-odd ($\mathcal{A}SD = \mathcal{A}PV$) and scalar $\mathcal{P}$, $T$-odd electron-nucleus interactions, and provide the corresponding expression within the ZORA in Table 2 (omitting the response terms). For detailed discussions of $P$-odd and $\mathcal{P}$, $T$-odd terms in quasirelativistic approximation see e.g. [21, 40] and [19, 41]. We use atomic units, unless otherwise stated.

The nuclear spin-dependent $P$-odd and scalar $\mathcal{P}$, $T$-odd operators in four-component formalism can be written as

$$H_{SD-PV} = \frac{G_F}{\sqrt{2}} \sum_{\lambda, i} k_{\Lambda \lambda} \hat{\alpha}(i) \cdot \hat{I}_{\lambda\alpha}(r_i),$$

$$H_{SP} = \frac{G_F}{\sqrt{2}} \sum_{\lambda, i} k_{SP, \Lambda} Z_A \gamma_0(i) \gamma_0(\rho_i) \hat{I}_{\lambda\alpha}(r_i),$$

where $G_F = 2.22254 \times 10^{-14}$ a.u. is Fermi’s constant of the weak interaction, $k_{\Lambda \lambda}$ is an effective parameter describing $\mathcal{A}SD - \mathcal{A}PV$ interactions for the nucleus $A$ (caused both by the nuclear anapole moment [42-44] and by weak electron-nucleon interactions [45]), $k_{SP, \Lambda}$ is a dimensionless coupling constant describing the scalar $\mathcal{P}$, $T$-odd interaction for nucleus $A$, $I_{\lambda\alpha}$ and $\rho_i$ are the spin and normalized nuclear density distribution of nucleus $A$, respectively, $\gamma_0$ and $\gamma_0$ are the Dirac $\gamma$-matrices and $\hat{\alpha}$ is a vector of Dirac’s $\alpha$-matrices. The summation runs over all nuclei $A$ and electrons $i$. In Table 2, $Q_A$ is the weak charge of nucleus $A$, $Q_A = N_A - (1 - 4 \sin^2 \theta_W) Z_A$, where $N_A$ is the number of neutrons in nucleus $A$, $Z_A$ stands for the nuclear charge, $\sin^2 \theta_W = 0.2319$, and $\hat{A}_{\hat{\mu}}$ is the magnetic vector potential from the point-like nuclear magnetic moments $\mu_A = \gamma_0 \hat{A}_{\hat{\mu}}$ with $\gamma_0 = \frac{1}{\gamma_0} = \frac{1}{\gamma_0} = \frac{1}{\gamma_0} = \frac{1}{\gamma_0}$, being the gyromagnetic ratio, $[x, y] = xy - yx$ is the anticommutator and $[x, y] = xy - yx$ is the commutator. The ZORA factor $\bar{\omega}$ is also used, $\bar{\omega} = 1/(2 - V/c^2)$, where $V$ is the model potential (with additional damping [46]) proposed in [47], which alleviates the gauge-dependence of the ZORA.

The $P$-odd nuclear spin-dependent and $\mathcal{P}$, $T$-odd scalar electron-nucleus contributions for the given nucleus $A$ (in our case the Ra nucleus) in paramagnetic diatomic molecules are described by the following terms of the effective molecular Hamiltonian [48, 49]:

$$W_{\lambda \lambda} \left[ \overset{\star}{\mathbf{S}} \cdot \hat{\mathbf{I}} \right] + W_{\lambda \lambda} \mathcal{P} \overset{\star}{\mathbf{S}} \cdot \hat{\mathbf{I}},$$

where $\hat{\mathbf{I}}$ is the unit vector directed from Ra to the OH group, $\overset{\star}{\mathbf{S}}$ is the effective electronic spin and $W_{\lambda \lambda}$ and $W_{\lambda \lambda}$ are parameters, which have to be deduced from electronic structure calculations. The physical meaning of the $W_{\lambda \lambda}$ parameter is $P$-odd hyperfine coupling constant [50], while $W_{\lambda \lambda}$ can be related to the parameters of $\mathcal{P}$, $T$-odd electron paramagnetic

Quasirelativistic calculations of $P$- and $P,T$-odd parameters

One of the popular quasirelativistic methods of electronic structure calculations is the ZORA method [34]. In contrast to the Breit–Pauli Hamiltonian, the ZORA Hamiltonian can be used in variational schemes (see [35] and references therein). Previously, we derived the expressions for matrix elements of the $P$-odd and $\mathcal{P}$, $T$-odd operators within the ZORA framework (see [19] and references therein) and related them to the corresponding effective operators in polyatomic open-shell molecules. Our previous calculations of $P$-odd nuclear spin-dependent and $\mathcal{P}$, $T$-odd properties for diatomic molecules within the generalized Hartree–Fock approach [19] were later confirmed in fully-relativistic four-component Hartree–Fock calculations [36, 37]. It turned out that the difference between the values of the $P$-odd parameters in the ZORA and four-component calculations does not exceed 5% (see [37]). Moreover, further studies by Gaul and Berger have demonstrated that even ‘purely-relativistic’ (depending only on small components of bispinors) $P$, $T$-odd properties, such as the enhancement of an electron permanent electric dipole

Figure 2. $\Delta \Pi_{1/2} - \chi^2 \Sigma_i_{1/2}$ transition value of the dipole moment operator $M$ as a function of $R_{Rao}$ according to D/C/FS-RCCSD calculations. Dashed line: longitudinal component $\Delta \Pi_{1/2,1/2}\Delta \Pi_{1/2,1/2}|\Delta \Pi_{1/2,1/2}|\Delta \Pi_{1/2,1/2}$; dotted line: transverse component $\Delta \Pi_{1/2,1/2}\Delta \Pi_{1/2,1/2}|\Delta \Pi_{1/2,1/2}|\Delta \Pi_{1/2,1/2}$; dash-dotted line: total transition dipole length $\Delta \Pi_{1/2,1/2}$, solid line corresponds to the spin-orbit-free $\Delta \Pi_{1/2,1/2}$ limit from the SF/FS-RCCSD calculations.
resonance. Measuring the shifts in molecular spin-rotational spectra due to the terms in (5) would allow the determination of e.g. nuclear anapole moment of Ra (see [41, 51] and references therein).

Our ZORA/GHF values (obtained for the equilibrium geometry from ARECP/MCSCF RaOH calculations) are $1.4 \times 10^3$ Hz for $W_s$ and $154 \times 10^3$ Hz for $W_c$. These values are rather close to the values of the corresponding parameters for RaF from [39, 41]. This is expected, since the main contribution to the regarded parameters in both cases originates from the unpaired electron located on the non-bonding molecular orbital, which is centered on Ra.

**Conclusion**

We propose RaOH as a polyatomic molecule containing a heavy nucleus, particularly suitable for highly effective cooling with lasers. Using the recently developed finite-field method, we calculate transition dipole moments for cooling transitions for RaOH and estimate Doppler limit temperature. For the first time, $\mathcal{P}$-odd and $\mathcal{P}$, $\mathcal{T}$-odd properties are calculated for a triatomic molecule with open electronic shells. Some other polyatomic molecules and ions with heavy nuclei may also be proposed for direct cooling with lasers according to the scheme proposed in our previous works, e.g. polyatomic analogs of TIF molecule (TICN etc) could be in principle considered as laser-coolable closed-shell molecules.

**Acknowledgments**

We are indebted to Professor R Berger for providing us with the code hotFCHT for calculations of FC factors in polyatomic molecules. TI is especially grateful to R Berger for numerous insightful discussions during joint work on the calculations of $\mathcal{P}$-odd and $\mathcal{P}$, $\mathcal{T}$-odd properties for molecules with open electronic shells and implementing the routines for the calculation of these properties within the tm2c code. We thank Dr Yu V Lomachuk and Dr Yu A Demidov for technical help. Financial support from RFBR (Grant Nos. 16-02-01064 and 16-03-00766) and computer time provided by the Center for Scientific Computing (CSC) Frankfurt, is gratefully acknowledged.

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**Table 2.** $\mathcal{P}$-odd and scalar $\mathcal{P}$, $\mathcal{T}$-odd terms in the ZORA Hamiltonian. Superscripts of $z$ denote orders of the corresponding ZORA terms on nuclear spin and $\mathcal{P}$-odd ($\mathcal{P}$, $\mathcal{T}$-odd ) coupling constants.

| Term | Name | Expression |
|------|------|------------|
| $z_{\mathcal{P}}^{(1,1)}$ | Scalar $\mathcal{P}$-odd interaction | $\frac{1}{2z^2} \{ \hat{\sigma} \cdot \hat{p} \cdot z \hat{p}_z \} $ |
| $z_{\mathcal{P}}^{(1,1)}$ | Scalar $\mathcal{P}$-odd / hyperfine P-even interaction | $\frac{1}{2z^2} \{ \hat{p} \cdot \hat{p}_z \} $ |
| $z_{\mathcal{P}}^{(1,1)}$ | Nuclear spin-dependent $\mathcal{P}$-odd interaction | $\frac{1}{2z^2} \{ \hat{p} \cdot \hat{p}_z \} $ |
| $z_{\mathcal{P}}^{(1,1)}$ | Nuclear spin-dependent $\mathcal{P}$-odd / hyperfine P-even interaction | $\frac{1}{2z^2} \{ \hat{p} \cdot \hat{p}_z \} $ |

Center for Scientific Computing (CSC) Frankfurt, is gratefully acknowledged.
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