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REGULAR ARTICLE

Reduced dipole pseudospectra for the accurate tabulation of C_6 dispersion coefficients

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Abstract The possibility of tabulating accurate reduced dipole pseudospectra of single molecules is of great importance for obtaining reliable dipole dispersion constants from which C_6 dispersion coefficients can be derived for all possible interacting pairs. Use of an efficient interpolation procedure allows to obtain dispersion constants from analytical integration of the Casimir–Polder integral over the product of frequency-dependent polarizabilities (FDPs) at imaginary frequencies. FDP calculations can then be done at a few selected frequencies, so overcoming at a time the difficulties arising from numerical quadratures and sensibly reducing the computational demand. In the static case, appropriately reduced n-term pseudospectra are obtained by forcing in an optimal way large N-term extended pseudospectra to be converted to FDPs using the same interpolation technique. Calculations performed at the eight frequencies arising by choosing $n = 4$ (four-term approximation) in the optimized interpolation procedure, give reduced dipole pseudospectra from which isotropic C_6 dispersion coefficients and γ_6 anisotropy coefficients are obtained in almost perfect agreement with the result of the most accurate data available from the literature and of recently proposed variational techniques.

Keywords Dispersion coefficients · Polarizability · Pseudospectra

1 Introduction

Uniform tabulation of long-range C_6 dispersion coefficients between interacting atoms and molecules is of great interest in the theoretical characterization of the asymptotic region of the potential energy surface. The attempt of obtaining *benchmark* calculations rests on the possibility of tabulating accurate reduced dipole pseudospectra of the individual molecules, from which C_6 dispersion coefficients can be readily derived for all possible interacting pairs [1].

2 Pseudospectra and dispersion coefficients

The N-term pseudospectrum $\{\alpha_i, \varepsilon_i\}$ $i = 1, 2, \ldots, N$ for molecule A is obtained from the *pseudospectral decomposition* of its polarizability, namely is the ordered set of N (non-observable) excited pseudostate contributions of each polarizability α_i with its own excitation energy ε_i to the total (observable) *static* polarizability α_a^{A}:

$$\alpha_a^{\mathrm{A}} = \sum_{i=1}^{N} \alpha_i. \tag{1}$$

In principle, and in practice, the pseudospectrum can be obtained in the simplest way through diagonalization of the matrix representative of the excitation energy operator $\left(\hat{H}_0 - E_0\right)$ over any convenient set of basis functions [1–3].

Knowledge of the pseudospectra of A and B allows the *direct* calculation of the C_{ab} dispersion constants for the A–B interacting pair in terms of the London formula [1]:

$$C_{ab} = \frac{1}{4}\sum_i \sum_j \alpha_i \alpha_j \frac{\varepsilon_i \varepsilon_j}{\varepsilon_i + \varepsilon_j} \tag{2}$$

where we have omitted for short the label (a, b) specifying polarizability and excitation energy contributions. The

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dispersion constants C_{ab} (with $a = b = 1$ for the dipole–dipole interaction) are the quantum mechanical part of the dispersion coefficients C_6, and arise from the coupling of the instantaneous interaction between fluctuating dipoles in the molecules. Better and better values for the C_{ab}s are obtained by increasing the number of pseudostates, the coupling between the interacting partners A and B in (2) occurring via the denominators $\varepsilon_i + \varepsilon_j$.

Relation to *frequency-dependent* polarizabilities (FDPs) is possible through the integral transform [1]:

$$\frac{1}{\varepsilon_i + \varepsilon_j} = \frac{2}{\pi}\int_0^\infty \mathrm{d}u \frac{\varepsilon_i}{\varepsilon_\mathrm{i}^2 + u^2}\frac{\varepsilon_j}{\varepsilon_j^2 + u^2} \quad \varepsilon_i, \varepsilon_j > 0 \tag{3}$$

giving for the dispersion constant (2) the *equivalent* Casimir–Polder expression [4]:

$$C_{ab} = \frac{1}{2\pi}\int_0^\infty \mathrm{d}u\ \alpha_a^\mathrm{A}(iu)\alpha_b^\mathrm{B}(iu). \tag{4}$$

Equation 4 involves integration over the (real) frequency u of the product of the FDPs of A and B evaluated at imaginary frequencies, i being the imaginary unit ($i^2 = -1$):

$$\alpha_a^\mathrm{A} = \sum_{i=1}^{N} \alpha_{ai} = \lim_{u \to 0} \alpha_a^\mathrm{A}(iu) \tag{5}$$

$$\alpha_b^\mathrm{B} = \sum_{j=1}^{N} \alpha_{bj} = \lim_{u \to 0} \alpha_b^\mathrm{B}(iu). \tag{6}$$

Values of the dipole dispersion constants were obtained in the past by our group using the static approach [5–7] and, more recently, by a joint work with the group of Professor Bendazzoli at the Physical Chemistry Department of the University of Bologna using the FDP technique [8–10]. Use of the London formula (2) for static polarizabilities seems preferable because the Casimir–Polder approach presents some problems in the accurate evaluation of the integral (4) through *numerical* quadrature techniques [1], which will be discussed later in this talk.

To give an example of the efficiency of the London procedure in an unequivocal case, 25-term pseudospectra with exact ψ_0 for H(1s) give C_{2n} values for H–H accurate to at least 16 significant figures up to $2n = 14$ [2], the value for C_6 being (atomic units are used throughout this paper):

$$C_6 = 6.499\ 026\ 705\ 405\ 839\ \mathbf{218}\cdots \tag{7}$$

which is seen to agree within 100×10^{-18} with the exact 20-decimal digits *benchmark of benchmarks* by Yan et al. [11]:

$$C_6 = 6.499\ 026\ 705\ 405\ 839\ 313\ 13\cdots \tag{8}$$

who used a Sturmian basis set containing up to 70 terms. Recently, Figari [12] did a 30-term pseudospectral calculation of the H(1s) static dipole polarizability, the actual limit of our numerical diagonalization technique, getting for C_6 a result which differs by only about 6×10^{-18} from the benchmark value (the last five figures being **307 50** instead of 313 13: five more terms in the pseudospectrum give one more *exact* figure in the 16th decimal place!).

3 How to obviate the difficulties of Casimir–Polder integration

To evaluate the Casimir–Polder integral (4) we must resort to some *numerical* quadrature technique, such as a 16- or 32-point Gauss–Legendre quadrature [13] or some modification of it as that originally suggested by Amos et al. [14] and used by Koch and Harrison [15] in their calculations on the Be atom, which allows to cover the whole integration range concentrating points in those regions where the integrand is larger. This is found to be particularly important when dealing with higher C_n dispersion coefficients such as the C_7 coefficients for LiH–LiH [16]. The need of a large number of integration points introduces further difficulties because increasing the number of frequencies at which the FDPs must be calculated increases greatly the computational demand, computation times being particularly severe near the zero-frequency. Furthermore, there are two conflicting necessities, (1) to have a large number of points near the zero-frequency, where $\alpha(iu)$ is larger, and at the same time, (2) to account properly for the tail of $\alpha(iu)$, which may decrease slowly, especially for the higher dispersion constants where higher multipoles are large far from the nucleus.

Progress was made along two directions.

(1) In 2003 we developed an elementary interpolation technique allowing to treat dispersion constants from FDPs through *analytical* calculations [17]. If the FDPs in the Casimir–Polder formula are represented by a truncated Sellmeier-type expansion in terms of a finite number n of parameters representing effective oscillator strengths and excitation energies, an efficient interpolation formula for the polarizabilities can be written as:

$$\alpha_a(iu) = \sum_{p=1}^{n} \frac{\sigma_p}{\tau_p + u^2} \quad n = 1, 2, \ldots \tag{9}$$

where τ_p and σ_p are adjustable parameters. Parameters optimization in the interpolation procedure follows from imposing a fully exact reproduction of $2n$ available values of the FDPs (α_1, α_2, …, α_{2n}) with evaluations performed at the known imaginary frequencies (iu_1, iu_2, …, iu_{2n}):

$$\sum_{p=1}^{n}\frac{\sigma_p}{\tau_p+u_1^2}=\alpha_1,\sum_{p=1}^{n}\frac{\sigma_p}{\tau_p+u_2^2}=\alpha_2,\ldots,\sum_{p=1}^{n}\frac{\sigma_p}{\tau_p+u_{2n}^2}=\alpha_{2n}. \tag{10}$$

Specific analytical formulae were derived for treating and directly solving the system of algebraic equations (10) resulting for $n \leq 4$ [17], determining in this way the best values of the $2n$ interpolation parameters σ_p and τ_p ($p = 1, 2, \ldots, n$). Substituting in (4), the Casimir–Polder integral can now be evaluated in *analytical* form in terms of the optimized parameters σ_p and τ_p as:

$$C_{ab}=\frac{1}{2\pi}\int_0^\infty \mathrm{d}u\ \alpha_a^{\mathrm{A}}(iu)\alpha_b^{\mathrm{B}}(iu)=\frac{1}{4}\sum_{p=1}^{n_a}\sum_{q=1}^{n_b}\frac{\sigma_p^a\sigma_q^b}{\sqrt{\tau_p^a\tau_q^b}\left(\sqrt{\tau_p^a}+\sqrt{\tau_q^b}\right)}. \tag{11}$$

Usually, a small set of interpolating parameters ($n \leq 4$) is found sufficient to yield high accuracy in the interpolation, provided frequencies are selected according to the formula [18]:

$$u_p=\frac{p-1}{2n+1-p}\quad (p=1,2,\ldots,2n). \tag{12}$$

In this way, the calculation of FDPs at a few selected points is sufficient to determine accurate values for the Casimir–Polder integral even far from the frequencies chosen.

(2) An alternative approach was recently introduced by Bendazzoli [19], who proposed a *variational* technique including upper and lower bounds to reduce the number of the frequencies involved. In his approach one expands the solution Φ_{AB} of the long-range Rayleigh–Schroedinger (RS) first-order perturbative equation in products of the perturbative solutions Φ_A and Φ_B for the separated molecules, using Hylleraas' principle to optimize the expansion coefficients (see also Kutzelnigg [20], and his theory of "natural asymptotic states of the interacting systems"). In order to compute the polarizabilities at the imaginary frequencies required by the conventional calculation, one solves the appropriate perturbative equations for molecule A and B separately getting solutions Φ_A and Φ_B which are in general complex. The latter or, better, their real (Re) and imaginary (Im) parts are used as expansion vectors to compute Φ_{AB}. The numerical quadrature of the Casimir–Polder integral corresponds to an expansion using the *real* part of the solutions Φ_A and Φ_B with non-variational coefficients. Therefore, the improvement of this approach can be ascribed to two factors, namely the variational optimization of the coefficients and the inclusion of the *imaginary* parts of Φ_A and Φ_B. The contribution of the latter is small, but not negligible, especially when a limited number of points is used. Recent calculations [10] of the dipole dispersion constants of BH–BH comparing four- and eight-term results show that the four-term values involving Re + Im are not far from the corresponding eight-term results, especially for the four-term lower bound, which shows noticeable fast convergence.

4 How to get uniformly *reduced* pseudospectra from either static or FDPs calculations

Conversion from the set of optimized interpolation parameters $\{\sigma_i, \tau_i\}$ to the n-term *reduced* pseudospectra $\{\alpha_i, \varepsilon_i\}$ was achieved using the equivalences [21]:

$$\alpha_i=\sigma_i/\tau_i,\ \varepsilon_i=\sqrt{\tau_i}. \tag{13}$$

The four-term approximation involving eight interpolation parameters (four linear σ_i and four non-linear τ_i coefficients) was found appropriate in adequately contracting the extended sets of source data.

For the frequency-dependent case, *reduced* pseudospectra were immediately obtained by performing FDP calculations at the eight frequencies that arise from putting $n = 4$ in the auxiliary formula (12).

In the static case, *reduced* n-term pseudospectra were obtained by forcing *large* N-term ($N > n$) extended pseudospectra to be converted to FDPs using the Figari–Magnasco interpolation technique at the eight frequencies selected according to formula (12).

Some source data for dipole polarizabilities available from literature are given in Table 1.

It is seen that the dimension of the accurately calculated pseudospectra for static dipole polarizabilities may be rather large, N being 25 for H(^{2}S) [2], 40 for He(^{1}S) [5],

Table 1 Source data for dipole polarizabilities available from literature

System	Data
H	25-term static pseudospectrum[a]
He	40-term static pseudospectrum[b]
Be	16 *u*-values for the FDP (full-electron calculation)[c]
H_2^+	27-term static pseudospectrum[d]
H_2	34-term static pseudospectrum[e]
LiH	32 *u*-values for each FDP (full-electron calculation)[f]
BeH_2	8 *u*-values for each FDP (frozen-core calculation)[g]
BH	8 *u*-values for each FDP (frozen-core calculation)[h]

[a] Magnasco et al. [2], [b] Magnasco and Ottonelli [5], [c] Koch and Harrison [15], [d] Magnasco and Ottonelli [6], [e] Magnasco and Ottonelli [7], [f] Bendazzoli et al. [8], [g] Bendazzoli et al. [9], [h] Bendazzoli et al. [10]

27 + 27 for either component (parallel and perpendicular) for $H_2^+(^2\Sigma_g^+)$ [6], and 34 + 34 for $H_2(^1\Sigma_g^+)$ [7]. 16 values of frequencies were used by Koch and Harrison [15] in their full-electron Full-CI calculations of the linear response functions on Be. 32 values of frequencies were used for the full-electron Full-CI calculation of each FDP component of LiH ($^1\Sigma^+$) [8] using a rather extended set of 109 Gaussian type orbitals (GTOs). However, Tunega and Noga [28] used a still larger basis set near saturation in their calculations of the static response properties of LiH. Eight selected imaginary frequencies were used for the FDPs calculations on $BeH_2(^1\Sigma_g^+)$ [9] and BH ($^1\Sigma^+$) [10], but for these molecules the large basis sets used in the calculations, 208 contracted GTOs for BeH_2 and 268 GTOs for BH, forced the use of a frozen-core approximation because, for instance, the dimensionality of the full-electron Full-CI space for BeH_2 was estimated to be about 270×10^9 Slater determinants and even more for BH, numbers that are far outside any possibility of the present computer capabilities.

Table 2 Four-term reduced dipole pseudospectra (atomic units) for atoms

α_i/a_0^3	ε_i/E_h
H	
$3.359\,341 \times 10^0$	$3.793\,741 \times 10^{-1}$
$9.981\,466 \times 10^{-1}$	$5.656\,096 \times 10^{-1}$
$1.378\,226 \times 10^{-1}$	$1.071\,940 \times 10^0$
$4.689\,923 \times 10^{-3}$	$2.811\,814 \times 10^0$
Be	
$3.663\,994 \times 10^1$	$1.957\,531 \times 10^{-1}$
$7.353\,711 \times 10^{-1}$	$5.865\,297 \times 10^{-1}$
$1.247\,698 \times 10^{-1}$	$1.975\,274 \times 10^0$
$3.112\,159 \times 10^{-2}$	$7.646\,136 \times 10^0$
He	
$7.071\,107 \times 10^{-1}$	$8.022\,210 \times 10^{-1}$
$4.977\,223 \times 10^{-1}$	$1.118\,638 \times 10^0$
$1.613\,181 \times 10^{-1}$	$1.910\,251 \times 10^0$
$1.675\,926 \times 10^{-2}$	$4.259\,569 \times 10^0$

Table 3 Four-term reduced dipole pseudospectra (atomic units) for homonuclear diatomics

α_i/a_0^3	ε_i/E_h
$H_2^+\parallel$	
$5.067\,316 \times 10^0$	$4.351\,008 \times 10^{-1}$
$4.944\,614 \times 10^{-3}$	$9.118\,537 \times 10^{-1}$
$4.323\,572 \times 10^{-3}$	$1.913\,057 \times 10^0$
$1.064\,524 \times 10^{-3}$	$4.252\,045 \times 10^0$
$H_2\parallel$	
$4.656\,280 \times 10^0$	$4.737\,530 \times 10^{-1}$
$1.501\,906 \times 10^0$	$6.657\,903 \times 10^{-1}$
$2.224\,207 \times 10^{-1}$	$1.083\,145 \times 10^0$
$2.073\,253 \times 10^{-3}$	$3.394\,450 \times 10^0$
$H_2^+\perp$	
$1.529\,475 \times 10^0$	$6.742\,115 \times 10^{-1}$
$1.841\,430 \times 10^{-1}$	$9.750\,040 \times 10^{-1}$
$4.184\,725 \times 10^{-2}$	$1.552\,454 \times 10^0$
$2.182\,900 \times 10^{-3}$	$3.522\,694 \times 10^0$
$H_2\perp$	
$2.909\,189 \times 10^0$	$4.954\,656 \times 10^{-1}$
$1.368\,299 \times 10^0$	$7.171\,300 \times 10^{-1}$
$2.866\,886 \times 10^{-1}$	$1.269\,471 \times 10^0$
$1.335\,458 \times 10^{-2}$	$2.948\,926 \times 10^0$

5 Results and discussion

The best four-term reduced pseudospectra resulting from our optimized calculations are given in Table 2 for atoms, Table 3 for homonuclear diatomics, and Table 4 for heteronuclear linear molecules. For the linear molecules, the dipole polarizabilities were evaluated at the minimum of the potential energy curves ($R = 2a_0$ for H_2^+, $R = 1.4a_0$ for H_2, $R = 3.015a_0$ for LiH, $R = 2.506a_0$ for BeH_2, $R = 2.329a_0$ for BH).

Table 5 collects the values of the C_{ab} dipole dispersion constants for all homo- and hetero-dimers resulting from the above four-term reduced dipole pseudospectra of the individual molecules for the ground states of H, He, Be, H_2^+, H_2, LiH, BeH_2, BH.

The C_6 dispersion coefficients are then obtained from the so-called L_AL_BM—scheme in terms of irreducible combinations of the elementary dispersion constants for the case of atom–atom, atom–linear molecule, and linear molecule–linear molecule interactions using the Tables given in Refs. [1, 22]. The isotropic $C_6 = C_6^{000}$ dispersion coefficients and the anisotropies $\gamma_6^{L_AL_BM} = C_6^{L_AL_BM}/C_6$ calculated therefrom are given in Table 6.

Accuracy in the results depends on the nature and completeness of the basis set and on the method of calculation.

The results from the static source are undoubtedly the most accurate, because they collect values from static polarizability calculations performed using either exact (H) or remarkably accurate wavefunctions for He, H_2^+, H_2. While details are left to the original papers [5–7], it will suffice to remind here that for the atomic or molecular two-electron systems the wavefunctions used in the calculation of either the unperturbed ground states or the excited pseudostates involve expansions in powers of coordinates including explicitly the interelectron distance r_{12}.

Absolute accuracy of the results from FDP sources is limited to some extent by the size of the basis set used (Be,

Table 4 Four-term reduced dipole pseudospectra (atomic units) for heteronuclear linear molecules

α_i/a_0^3	ε_i/E_h
LiH∥	
$1.695\,591 \times 10^{1}$	$1.449\,226 \times 10^{-1}$
$8.409\,862 \times 10^{0}$	$3.735\,047 \times 10^{-1}$
$6.437\,668 \times 10^{-1}$	$1.009\,690 \times 10^{0}$
$1.233\,306 \times 10^{-1}$	$3.611\,446 \times 10^{0}$
BeH_2∥	
$1.471\,246 \times 10^{1}$	$3.631\,637 \times 10^{-1}$
$4.474\,225 \times 10^{0}$	$5.374\,278 \times 10^{-1}$
$7.431\,079 \times 10^{-1}$	$9.990\,290 \times 10^{-1}$
$1.092\,569 \times 10^{-2}$	$3.499\,773 \times 10^{0}$
BH∥	
$1.248\,248 \times 10^{1}$	$2.627\,887 \times 10^{-1}$
$9.384\,623 \times 10^{0}$	$4.506\,600 \times 10^{-1}$
$1.113\,820 \times 10^{0}$	$9.923\,927 \times 10^{-1}$
$3.544\,974 \times 10^{-2}$	$6.061\,755 \times 10^{0}$
LiH⊥	
$2.446\,670 \times 10^{1}$	$1.751\,053 \times 10^{-1}$
$4.648\,334 \times 10^{0}$	$4.023\,576 \times 10^{-1}$
$4.505\,748 \times 10^{-1}$	$1.184\,342 \times 10^{0}$
$1.282\,684 \times 10^{-1}$	$3.595\,837 \times 10^{0}$
BeH_2⊥	
$1.425\,507 \times 10^{1}$	$3.232\,516 \times 10^{-1}$
$4.566\,497 \times 10^{0}$	$5.348\,032 \times 10^{-1}$
$8.188\,295 \times 10^{-1}$	$1.065\,332 \times 10^{0}$
$2.965\,019 \times 10^{-2}$	$2.958\,492 \times 10^{0}$
BH⊥	
$6.787\,413 \times 10^{0}$	$1.170\,582 \times 10^{-1}$
$1.247\,128 \times 10^{1}$	$4.147\,770 \times 10^{-1}$
$1.334\,336 \times 10^{0}$	$1.016\,659 \times 10^{0}$
$4.410\,018 \times 10^{-2}$	$5.605\,912 \times 10^{0}$

Table 5 C_{ab} dipole dispersion constants ($E_h a_0^6$) for homo- and hetero-dimers from four-term reduced pseudospectra

System	C_{ab}	System	C_{ab}	System	C_{ab}
H–H	1.083	Be–LiH⊥	28.327	H_2∥–BH⊥	6.431
H–He	0.470	Be–BeH_2∥	25.322	H_2⊥–H_2⊥	1.542
H–Be	5.790	Be–BeH_2⊥	24.306	H_2⊥–LiH∥	4.789
H–H_2^+∥	1.234	Be–BH∥	27.510	H_2⊥–LiH⊥	5.312
H–H_2^+⊥	0.531	Be–BH⊥	22.845	H_2⊥–BeH_2∥	5.529
H–H_2∥	1.698	H_2^+∥–H_2^+∥	1.405	H_2⊥–BeH_2⊥	5.229
H–H_2⊥	1.276	H_2^+∥–H_2^+⊥	0.604	H_2⊥–BH∥	5.816
H–LiH∥	4.217	H_2^+∥–H_2∥	1.933	H_2⊥–BH⊥	4.820
H–LiH⊥	4.711	H_2^+∥–H_2⊥	1.452	LiH∥–LiH∥	17.796
H–BeH_2∥	4.706	H_2^+∥–LiH∥	4.798	LiH∥–LiH⊥	20.087
H–BeH_2⊥	4.467	H_2^+∥–LiH⊥	5.360	LiH∥–BeH_2∥	18.410
H–BH∥	4.992	H_2^+∥–BeH_2∥	5.359	LiH∥–BeH_2⊥	17.624
H–BH⊥	4.130	H_2^+∥–BeH_2⊥	5.087	LiH∥–BH∥	19.887
He–He	0.243	H_2^+∥–BH∥	5.685	LiH∥–BH⊥	16.530
He–Be	2.203	H_2^+∥–BH⊥	4.700	LiH⊥–LiH⊥	22.716
He–H_2^+∥	0.533	H_2^+⊥–H_2^+⊥	0.276	LiH⊥–BeH_2∥	20.582
He–H_2^+⊥	0.255	H_2^+⊥–H_2∥	0.853	LiH⊥–BeH_2⊥	19.728
He–H_2∥	0.767	H_2^+⊥–H_2⊥	0.650	LiH⊥–BH∥	22.291
He–H_2⊥	0.591	H_2^+⊥–LiH∥	1.953	LiH⊥–BH⊥	18.522
He–LiH∥	1.678	H_2^+⊥–LiH⊥	2.158	BeH_2∥–BeH_2∥	20.451
He–LiH⊥	1.840	H_2^+⊥–BeH_2∥	2.297	BeH_2∥–BeH_2⊥	19.425
He–BeH_2∥	2.027	H_2^+⊥–BeH_2⊥	2.168	BeH_2∥–BH∥	21.720
He–BeH_2⊥	1.908	H_2^+⊥–BH∥	2.405	BeH_2∥–BH⊥	17.966
He–BH∥	2.109	H_2^+⊥–BH⊥	1.995	BeH_2⊥–BeH_2⊥	18.467
He–BH⊥	1.757	H_2∥–H_2∥	2.689	BeH_2⊥–BH∥	20.670
Be–Be	35.417	H_2∥–H_2⊥	2.032	BeH_2⊥–BH⊥	17.102
Be–H_2^+∥	6.589	H_2∥–LiH∥	6.451	BH∥–BH∥	23.163
Be–H_2^+⊥	2.613	H_2∥–LiH⊥	7.173	BH∥–BH⊥	19.172
Be–H_2∥	8.765	H_2∥–BeH_2∥	7.365	BH⊥–BH⊥	15.905
Be–H_2⊥	6.467	H_2∥–BeH_2⊥	6.973		
Be–LiH∥	24.996	H_2∥–BH∥	7.768		

LiH) and by the need of introducing the frozen-core approximation (BeH_2 and BH). A further limit in the present values concerning Be and LiH arises from the fact that the four-term interpolation for these molecules was forced to use frequencies falling outside the reference set determined by Eq. 12. These limits, however, are all inherent to restrictions in the quality of the wavefunctions used in the calculations and *not* in the general method of obtaining reduced pseudospectra discussed in this talk. Improvement is always possible by improving the quality of the wavefunctions, so that revision of the data given in Table 6 is possible at any moment.

To give an idea of the accuracy resulting from our method, we compare in Table 7 the most reliable source literature data derived from accurate static calculations on the most simple one- and two-electron atomic and molecular systems with the results of our four-term reduced pseudospectra. It can be seen that the majority of the data reported here are accurate to at least the third decimal figure, and sometimes even more.

Lastly, we want to touch upon a point that is actually object of current research in our group. When the number M of available polarizability evaluations exceeds the required minimum number $2n$ needed for the n-term interpolation (Eq. 10), the remaining $M - 2n$ data can be used to improve the efficiency of the interpolation result by minimizing the expression:

$$\sum_{q=1}^{M}\left(\sum_{p=1}^{n}\frac{\sigma_p}{\tau_p+u_q^2}-\alpha_q\right)^2 \qquad M \geq 2n. \tag{14}$$

Solution of the algebraic system of $2n$ equations resulting from minimization of (14) is obtained numerically using the Newton–Raphson method [26] in a

Table 6 C_6 isotropic dispersion ($E_h a_0^6$) and γ_6 anisotropy coefficients for homo- and hetero-dimers from four-term reduced pseudospectra

System	C_6	γ_6^{020}	γ_6^{200}	γ_6^{220}
H–H	6.499			
H–He	2.821			
H–Be	34.739			
$H–H_2{}^+$	4.591	0.306		
$H–H_2$	8.502	0.099		
H–LiH	27.279	−0.036		
$H–BeH_2$	27.281	0.017		
H–BH	26.503	0.065		
He–He	1.460			
He–Be	13.220			
$He–H_2{}^+$	2.085	0.267		
$He–H_2$	3.899	0.090		
He–LiH	10.717	−0.030		
$He–BeH_2$	11.688	0.020		
He–BH	11.246	0.063		
Be–Be	212.503			
$Be–H_2{}^+$	23.630	0.337		
$Be–H_2$	43.401	0.106		
Be–LiH	163.299	−0.041		
$Be–BeH_2$	147.866	0.014		
Be–BH	146.401	0.064		
$H_2{}^+–H_2{}^+$	3.284	0.296	0.296	0.289
$H_2{}^+–H_2$	6.096	0.097	0.294	0.091
$H_2{}^+$–LiH	18.705	−0.035	0.330	−0.038
$H_2{}^+–BeH_2$	19.199	0.018	0.309	0.015
$H_2{}^+$–BH	18.584	0.065	0.312	0.062
$H_2–H_2$	11.324	0.096	0.096	0.029
H_2–LiH	34.416	−0.034	0.104	−0.012
$H_2–BeH_2$	35.525	0.019	0.100	0.005
H_2–BH	34.360	0.065	0.100	0.020
LiH–LiH	126.006	−0.040	−0.040	0.005
$LiH–BeH_2$	115.823	0.014	−0.037	−0.001
LiH–BH	114.412	0.063	−0.037	−0.007
$BeH_2–BeH_2$	114.679	0.017	0.017	0.001
BeH_2–BH	111.600	0.065	0.017	0.003
BH–BH	108.980	0.064	0.064	0.013

convenient matrix form. Preliminary applications to the first three polarizabilities of the H atom ground state [27] show that the accuracy of the four-term interpolation for all possible resulting (11, 21, 22, 31, 32, 33) dispersion constants is significantly improved, giving a difference from the exact result of no more than one digit in the last of eight significant figures irrespective of the multipole considered.

Table 7 Comparison with accurate literature results (atomic units) of isotropic dipole polarizabilities α and C_6 dispersion coefficients for homodimers from best four-term reduced pseudospectra obtained from static data

	α/a_0^3		$C_6/E_h a_0^6$	
He	1.382_9	1.383_2^a	1.460_3	1.460_9^a
$H_2{}^+$	2.864_3	2.864_3^b	3.283_6	3.283_6^b
H	4.5	4.5^a	6.499_0	6.499_0^a
H_2	5.179_2	5.178_6^c 5.181_5^d	11.324_3	11.324_3^e

[a] Yan et al. [11]: 504-term $\psi_0(^1S)$ and 728-term $\psi_1(^1P)$

[b] Babb [23]: 40-term $\psi_0\left(^2\Sigma_g^+\right)$, 48-term $\psi_1(^2\Sigma_u^+)$and $\psi_1(^2\Pi_u)$

[c] Kołos and Wolniewicz [24]: 54-term $\psi_0\left(^1\Sigma_g^+\right)$, 34-term $\psi_1(^1\Sigma_u^+)$ and $\psi_1(^1\Pi_u)$

[d] Bishop et al. [25]: 249-term $\psi_0\left(^1\Sigma_g^+\right)$, 113-term $\psi_1(^1\Sigma_u^+)$, and 190-term $\psi_1(^1\Pi_u)$

[e] Magnasco and Ottonelli [7]: 54-term $\psi_0\left(^1\Sigma_g^+\right)$, 34-term $\psi_1(^1\Sigma_u^+)$ and $\psi_1(^1\Pi_u)$

6 Conclusions

Using our interpolation procedure [17] optimized *reduced* four-term pseudospectra [1] were readily derived for those atomic or molecular systems whose static or dynamic polarizabilities are available from source literature data [2, 5–10, 15]. The four-term approximation, involving eight interpolation parameters evaluated by performing FDP calculations at the eight frequencies that arise from putting $n = 4$ in the auxiliary formula (12), was found appropriate in adequately contracting the extended set of FDP source data. In the static case, *reduced* four-term pseudospectra were obtained by forcing *large* *N*-term extended pseudospectra to be converted to FDPs using the Figari–Magnasco interpolation technique [17] at the same eight frequencies.

Accuracy in the final four-term pseudospectra presented here depends just on the nature and completeness of the basis set and on the approximations in the wavefunctions. Results from *static* source data are believed to be the most accurate to date for the tabulation of reliable dispersion coefficients and anisotropies, but revision of less accurate results is always possible when improving the quality of the wavefunctions of the constituent molecules.

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