A Quasi-Universal Internuclear Potential Energy Function for the Diatomic Halides

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Taking into account the universal correlation of the force constants of halide bonds with their respective dissociation energies (excluding the fluorides), an internuclear potential energy function of the type

$$V(r) = D_e(1 - e^{-\alpha(r-r_e)})^2 + \beta(1 - \delta_{F,X})(r - r_e)^2 e^{-\gamma(r-r_e)}$$

has been proposed for the diatomic halides. α und β, in the latter are constants for a specific series, γ is determined from the rotational-vibrational constant α_e, and the function reduces to the ordinary Morse potential function in the case of the fluorides. It, moreover, performs as well as the Hulburt-Hirschfelder 5-parameter function, and, unlike the latter, utilizes the anharmonicity constant $\omega_e x_e$ as an internal check.

Introduction

In a previous study[1] we presented a generalized formula of the type $Y = K\omega + C$ in which ω was given as a function of the electronegativity difference of the atoms forming the MX (halide) bond and which was simultaneously applicable to the stretching force constants, the bond dissociation energies, the thermochemical bond energies, as well as the reciprocals of the mean square quantities σ_r of the halides. The specific expressions for the aformentioned correlations, moreover, were given by

(i) $f_r(\text{md/Å}) = m' X + C$

(ii) D_e or E (kcal-mole^{-1}) $= m''(X + a\,\delta_{F,X}) + C''$

$$\begin{cases} a \simeq -15 \text{ for } \chi_M > 1 \\ a \simeq -30 \text{ for}^* \chi_M < 1 \end{cases}$$

and

(iii) $\sigma_r^{-1}(\text{Å}^{-2}) = m'''(X + b\,\delta_{F,X}) + C'''$, $b \simeq -11$

where $\delta_{F,X}$ was the kronecker delta and X, the Hannay-Smyth relation[2], was given by

$$X = 16(\chi_M - \chi_X)^2 + 3.5\,|\chi_M - \chi_X|,$$

χ_M and χ_X being the Pauling electronegativities[3] of the atoms forming the MX bond.

A very interesting outcome of the said investigation was also the fact that for *all* MX_n type halide molecules (*excluding the fluorides*), irrespective of geometric configuration, position of M in the periodic table, and the extent of "hybridization" of orbitals on M, a linear correlation was always found between the bond dissociation energies (Or alternatively the thermochemical bond energies) and the stretching force constants f_r of a given series of halides. In fact, the evidence was so overwhelming that it prompted us to search for a universal internuclear potential energy function which not only was a fit to the experimentally obtained curves, but also reflected these observed, and indeed what seems to us, fundamental interrelations in a given halide series. (Henceforth the phrase "halide series," unless specifically stated, will mean the series *excluding* the fluorides.)

The present paper is an attempt in that direction and deals specifically with the simplest of the halides, the diatoms. However, before proceeding with our discussion it is instructive to mention that the general subject of empirical potential functions for diatomic molecules has been discussed extensively in two review papers, one by VARSHNI[4] and the other by STEELE et al.[4a]. Nonetheless, we would like to make the following additional remarks:

(i) By considering a large number of diatomic molecules (see Table I), it was found that the "average" percentage error in α_e, the vibrational-rotational constant, and in $\omega_e x_e$, the anharmonicity

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[1] W. A. YERANOS, J. Chem. Phys. **50**, 3670 [1969].

[*] In the case of NaX $a = -15$. See Ref.[1] for details.

[2] N. B. HANNAY and C. P. SMYTH, J. Amer. Chem. Soc. **68**, 171 [1946].

[3] P. ANDER and J. SONNESSA, Principles of Chemistry, The Macmillan Co., New York 1965.

[4] Y. P. VARSHNI, Rev. Mod. Phys. **29**, 664 [1957].

[4a] D. STEELE, E. R. LIPPINCOTT, and J. T. VANDERSLICE, Rev. Mod. Phys. **34**, 329 [1962].

constant, calculated by both the Varshni III [5] and Lippincott functions [5] were indeed comparable and there was no reason to believe that one was better than the other in the estimation of these parameters.

(ii) It was found that although it is true that the 5-parameter HULBURT-HIRSCHFELDER [6] function is applicable in the region of interest to spectroscopists, it nonetheless does not always satisfy one of the important conditions of an acceptable internuclear potential, namely that of becoming very large as the internuclear distance becomes small. In the case of BBr, for instance, the potential at 0.025 Å is — 125.63 e.v (D_e taken as zero). It rises to 103.65 e.v. at 0.35 Å, and then follows the usual Morse-type pattern. Even the alternate function [6a] suggested by Hulburt and Hirschfelder did not perform better and gave a maximum at an internuclear separation of about 0.2 Å.

(iii) Varshni's conclusions that no three-constant universal potential energy can be found, is succinctly demonstrated by a plot of D_e v/s f_r. Indeed, from Fig. 1 one readily sees that no correlation between D_e and f_r exists, while Fig. 2 indicates that such correlations do exists for the diatomic halides (this is valid for both the diatomic and polyatomic halides). An examination of the latter, moreover, reveals that for *all* halide series one has the following type of relationships

$$f_r = m\,D_e + C$$

where f_r is the stretching force constant, D_e the dissociation energy of the MX bond, and m and C are specific constants for a particular series.

This, in fact, was expected. It should be recalled that we had prevoiusly [1] shown that in any halide series, and to a very good degree of approximation, one had

$$f_r = m'\,X + C'$$

and

$$D_e = m''\,(X + a\,\delta_{F,X}) + C''.$$

Combining the above equations, we obtain

$$f_r = \frac{m'}{m''}\,D_e + \left(C' - a\,\delta_{F,X}\,m' - \frac{m'}{m''}\,C''\right) = m\,D_e + C\,.$$

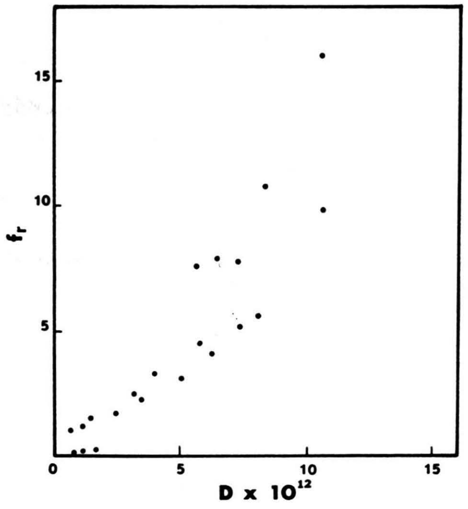

Fig. 1. Force constants f_r (md/Å) of most of the molecules studied by Varshni versus the dissociation energy D (erg).

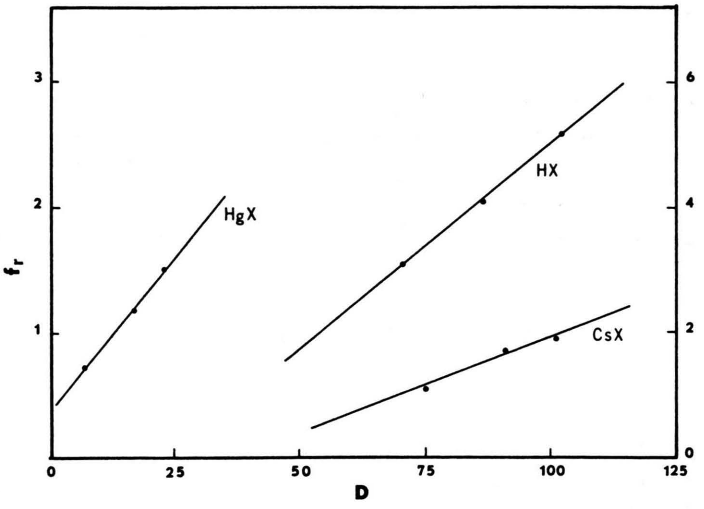

Fig. 2. Force constants f_r (md/Å) of some halides versus the dissociation energy D (e.v.). The choice reflects a wide range of electronegativities of M.

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[5] The $\omega_e x_e$ expression using the Varshni III function seems to be incorrectly given by VARSHNI [4]. The fourth derivative of this function as derived by us is

$$V^{iv}(r_e) = D_e(72\,r_e^{-4} + 192\,\alpha\,r_e^{-2} + 216\,\alpha^2 + 160\,\alpha^3\,r_e^2 + 224\,\alpha^4\,r_e^4)$$

while as derived by Varshni himself seems to be

$$V^{iv}(r_e) = D_e(72\,r_e^{-4} + 172\,\alpha\,r_e^{-2} - 24\,\alpha^2 + 160\,\alpha^3\,r_e^2 + 224\,\alpha^4\,r_e^4).$$

The correctness of our expression has been verified by Dr. ALAN ADLER and Mr. HARRY MILLER of this laboratory to whom the author is indebted.

[6] H. M. HULBERT and J. O. HIRSCHFELDER, J. Chem. Phys. **9**, 61 [1941].

[6a] This function (Eq. [18] of Ref. [6]) was suggested to correct a similar difficulty encountered in the potential energy curve of Cl_2 obtained by the standard Hulburt and Hirschfelder function.

Mol.	a*	% ε in α_e		% ε in $\omega_e x_e$	
		L	V-III	L	V-III
H_2	0.294	−21.7	40.3	4.5	27.5
ZnH	0.600	59.8	52.4	32.6	39.2
CdH	0.619	55.6	49.7	56.1	65.7
HgH	0.660	60.4	58.9	45.9	58.9
CH	0.466	− 8.3	− 6.5	− 6.2	− 4.5
OH	0.473	− 7.3	− 6.4	− 1.3	0.3
HF	0.431	−22.8	−16.0	−19.0	−16.5
HCl	0.491	− 5.2	− 6.5	− 2.1	− 0.7
HBr	0,513	2.9	− 0.6	3.3	5.0
HI	0.539	0.5	− 4.3	8.4	10.8
Li_2	0,481	32.0	31.9	17.3	19.3
Na_2	0.515	65.3	59.4	19.3	21.4
K_2	0.553	66.9	58.3	15.7	18.8
P_2	0.587	9.5	3.9	4.5	8.9
O_2	0.569	− 1.2	− 6.4	− 0.9	2.5
SO	0.598	13.0	7.6	24.4	30.4
Cl_2	0.614	− 1.7	− 5.7	−22.9	−18.4
Br_2	0.633	34.4	30.4	10.4	18.3
I_2	0.649	14.9	12.8	15.7	25.6
ICl	0.623	6.7	2.9	7.9	14.8
N_2	0.554	− 0.8	− 5.9	2.8	5.7
CO	0.510	−16.8	−19.5	−22.2	−20.9
NO	0.562	− 2.6	− 7.8	− 4.0	− 1.2
BBr	0.508	−16.5	−19.0	−25.9	−24.7
BCl	0.499	−31.3	−32.8	−32.4	−31.3
BF	0.461	−36.2	−34.5	−45.3	−44.3
AlBr	0.511	−33.3	−35.4	−32.2	−36.7
AlCl	0.489	−54.2	−54.8	−41.2	−40.2
InCl	0.494	−62.9	−63.5	−43.4	−42.5
"Average** % error"		±24.3	±18.7	±23.9	±21.9

* a of the Lippincott function is given by $a = 4/5\,(1 - \Delta^{-1/2} b^{-1})$ where $\Delta = f_r\, r_e^2/2\, D_e$.
** This average does not include the parameters for InCl.

Table I. Percentage Errors in α_e and $\omega_e x_e$ Using the Lippincott (L) and Varshni III (V-III) Potential Functions.

Mathematical Formulation

Clearly, then, the previously mentioned relationship of the force constants with the dissociation energies suggests that the potential energy of the diatomic halides could, in its simplest form, be given by the general expression

$$V(r) = F(r)\, D_e + G(r)$$

such that

$$V''(r_e) = F''(r_e)\, D_e + G''(r_e)$$

and where $V(r)$ must, as a minimum, satisfy the following conditions:

(i) $V(r) \to D_e$ as $r \to \infty$,
(ii) $V(r) \to$ very large, $r \to$ very small,
(iii) $V'(r_e) = 0$

and

(iv) $V''(r_e) \equiv f_r$.

A simple and acceptable form of $G(r)$ was found by us to be

$$G(r) = \beta (1 - \delta_{F,X})\,(r - r_e)^2 \exp\{-\gamma (r - r_e)\}$$

where β and γ are constants and $\delta_{F,X}$ is the kronecker delta. Furthermore, for the diatomic halides, the following possible forms of $F(r)$ were conidered[7]

(i) $[1 - \exp\{-\alpha (r - r_e)\}]^2$ (Morse-type)
(ii) $[1 - (1 + \alpha) \exp\{-\alpha (r - r_e)\}]$ (Rydberg-type)
(iii) $[1 - r_e/r \exp\{-\alpha (r^2 - r_e^2)\}]^2$ (Varshni III-type)

It should be noted that all combinations of these forms of $F(r)$ and $G(r)$ satisfy the previously stated conditions. They, furthermore, give as required, the following type expressions

$$f_r = F''(r_e)\, D_e + 2\beta\,.$$

In the case of the Morse-type function, for instance, we have

$$f_r = 2\alpha^2 D_e + 2\beta\,,$$

where α and β can easily be determined when the force constants and the dissociation energies of any two halides are known. The latter, it goes without saying, are the most easily accessible, in as far as tabulated data is concerned, spectroscopic parameters.

The specific value of any γ in $G(r)$, on the other hand, was determinable from the expression of the rotational-vibrational constant α_e given[8] by

$$\alpha_e = -\left[\frac{1}{3}\left(\frac{V'''(r_e)}{V''(r_e)}\right) r_e + 1\right] \frac{6\, B_e^2}{\omega_e}$$

while the "goodness of fit" of any particular curve was assessed by

(i) The percentage error of the calculated anharmonicity constant $\omega_e x_e$ obtained by

$$\omega_e x_e = \left[\frac{5}{3}\left(\frac{V'''(r_e)}{V''(r_e)}\right)^2 - \left(\frac{V^{iv}(r_e)}{V''(r_e)}\right)\right] \frac{W}{\mu_A}$$

as compared to the experimental values, and

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[7] Because of the unknown effect of our modification on the b constant in the Lippincott function[5], the latter was not included in our search of a suitable $F(r)$ function.

[8] In the following two expressions, all symbols have their usual spectroscopic meanings as given by HERZBERG (Table 39 of Ref.[9]).
$W = \hbar N/32\,\pi c = 2.1078 \times 10^{-16}$ gm-cm.

[9] G. HERZBERG, Spectra of Diatomic Molecules, Van Nostrand Co., Inc., Princeton, New Jersey 1967.

(ii) The average percentage deviation of the curves from the 5-parameter potential. Unfortunately, since only the lowest few vibrational levels of the diatomic halides[10] are known, the RYDBERG-KLEIN-REES[12] analytical method was not applicable and consequently the second-best choice, the Hulburt-Hirschfelder potential was used for the simulation of the experimental curves. (Bearing in mind, the point raised in the Introduction with respect to the shortcomings of this function.)

Results and Discussion

Of the one hundred and forty-one diatomic halide molecules reported by HERZBERG[9], it is unfortunate that the internuclear distance, without which no potential function can be established, of only thirty-one of them are known. To make things even worse, only eleven of the latter, or approximately eight per cent of the total number of halides, have the minimum information necessary for any adequate analysis[13]. When one adds to this also the fact that the α_e values of AlCl and InCl are the roughest estimates of the entire Herzberg compilation[14], one is then left with only the following series for study

(i) HI, HBr, HCl, HF,
(ii) AlBr
and (iii) BBr, BCl, BF.

Confronted with this scarcity of adequate experimental data, we chose to use the hydrogen halides as "prototypes" and hoped to be able to transfer all pertinent conclusions reaches in the study of this series to the remaining molecules of the above set. Table II gives the percentage errors in the rotational-vibrational and anharmonicity constants of the hydrogen halides using the Morse (M), the Rydberg (R), and the Varshni III (V-III) functions, while Table III gives the said errors in our modified forms of the same functions. An examination of the latter indicates that when the fluoride is included the best modified form is given by

$$V(r) = D_e\,[1 - \exp\{-\alpha(r - r_e)\}]^2 + \beta(1 - \delta_{F,X})\,(r - r_e)^2 \exp\{-\gamma(r - r_e)\}\,.$$

	% error in α_e			% error in $\omega_e x_e$		
	M	R	V-III	M	R	V-III
HI	14.1	4.1	− 4.3	35.7	24.4	10.8
HBr	16.4	5.7	− 0.6	28.0	17.4	5.0
HCl	6.8	− 3.6	− 6.5	19.8	9.8	− 0.7
HF	−16.3	−25.9	−16.0	− 2.4	−10.2	−16.5

Table II. Percentage errors in α_e and $\omega_e x_e$ of the halides using the Standard $F(r)$ functions considered in this study.

	% error in α_e			% error in $\omega_e x_e$		
	Y-M	Y-R	Y-V-III	Y-M	Y-R	Y-V-III
HI	0.0	0.0	0.0	20.1	20.5	20.1
HBr	0.0	− 1.7	− 1.7	17.4	12.4	7.2
HCl	0.0	0.0	0.0	12.2	13.1	7.6
HF	−16.3	−25.9	−16.0	− 2.4	−10.2	−16.5

Table III. Percentage errors in α_e and $\omega_e x_e$ of the halides using our modified forms of the potential functions considered in this study.

Fig. 3 shows the potential energy curve of HBr obtained from the above equation as compared to the curve obtained by the 5-parameter function. As can be seen the fit seems to be perfect although the percentage error in the anharmonicity constant[15] is found to be 17.4. It should be noted that the values of α in (Å^{-1}) and β (in e.v.-Å^{-2}) for the series were obtained respectively from the slope m and the intercept C of the f_r(md/Å) v/s D_e(e.v.) curve[16] of the latter. That is from

$$m = 2\alpha^2 = 6.242\,Q$$

and

$$C = 2\beta = 6.242\,[f_r(\mathrm{HCl}) - Q \cdot D_e(\mathrm{HCl})]$$

where

$$Q = [f_r(\mathrm{HCl}) - f_r(\mathrm{HI})]/[D_e(\mathrm{HCl}) - D_e(\mathrm{HI})]$$

1 md = 6.242 e.v.-Å^{-1}.

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[10] Although the fluorides, as mentioned earlier, are excluded, the complete R.K.R. curve of only HF is to date available[11].

[11] R. J. FALLON, J. T. VANDERSLICE, and E. A. MASON, J. Chem. Phys. **32**, 698 [1960]; **33**, 944 [1960].

[12] R. RYDBERG, Z. Physik, **73**, 376 [1931]; **80**, 514 [1933]; O. KLEIN, Z. Physik, **76**, 221 [1932]; A. L. G. REES, Proc. Phys. Soc. London **59**, 998 [1947].

[13] These are the five spectroscopic parameters ω_e, D_e, α_e, and $\omega_e x_e$. We would like to point out here that only in extremely rare cases is r_e known without a knowledge of α_e.

[14] The α_e values of AlCl and InCl are the only ones in the entire Herzberg compilation that are given to one significant figure. Both the 5-parameter and our suggested (see later) functions seem to be quite sensitive to the accuracy of α_e. In fact, in the case of InCl, for instance, the 5-parameter function gives a maximum, similar to predissociation, at about 5.3 Å and does not converge to the dissociation limit.

[15] This seeming contradiction was pointed out by STEELE et al.[5].

[16] All data used in this project were obtained from Herzberg's compilation (Ref.[9]), except the dissociation energy of HF which was taken from Ref.[5].

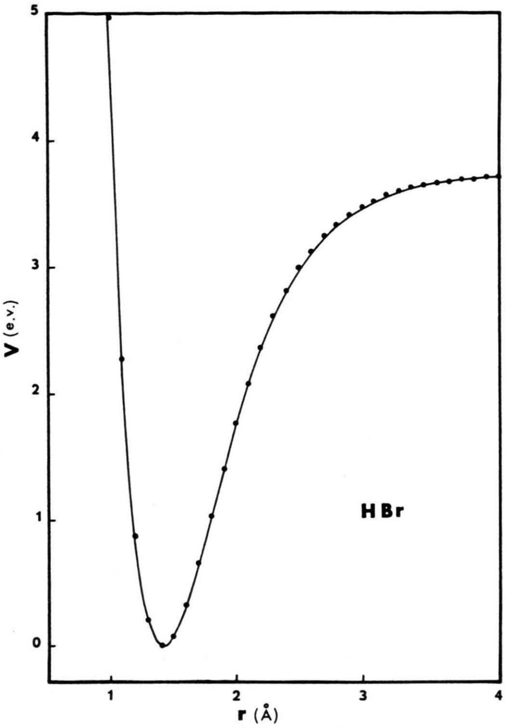

Fig. 3. Potential energy curve of HBr using our suggested potential. The circles represent the curve traced by the 5-parameter function.

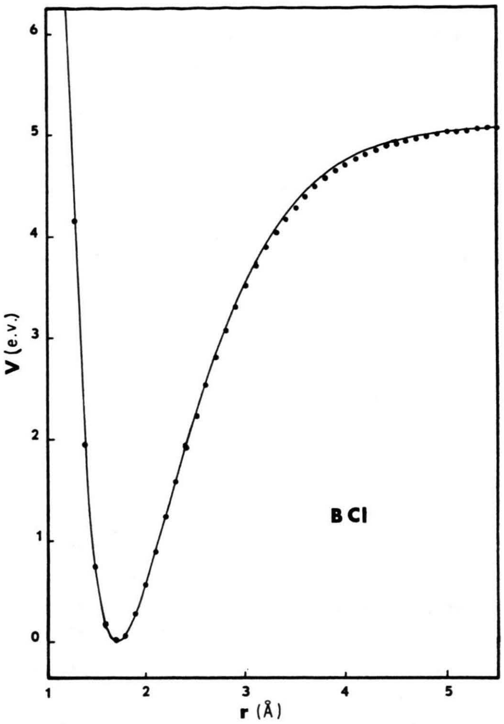

Fig. 4. Potential energy curve of BCl using our suggested potential. The circles represent the curve traced by the 5-parameter function.

The specific values of γ (in Å^{-1}) for each member of the series, on the other hand, were determined from the rotational-vibrational constants. Substituting the explicit forms of the derivatives[17] of the above suggested potential in the expression for α_e, and after proper unit conversions, one obtains

$$\gamma = \left[\frac{3.121\, f_r}{r_e}\left(1 + \frac{\alpha_e\, \omega_e}{6\, B_e^2}\right) - \alpha^3 D_e\right] \Big/ \beta\,.$$

Table IV gives the calculated parameters of all the halides considered in this study, while Fig. 4 shows the potential energy curve of BCl obtained from the proposed function. Here again, the fit seems to be rather good.

We conclude this report by reemphasizing that, in as far as the diatomic halides were concerned, the primary aim of the present investigation was to develop a function which reflected the unquestionable correlation of the dissociation energies of these molecules with their respective force constants. Needless to say, we also endeavored to propose a function which compared favorably with what is generally accepted as the best empirical function — the Hulburt-Hirschfelder function. The suggested function not only performs as well as the 5-parameter function, but unlike the latter, uses only four of the usual parameters (ω_e, D_e, r_e, α_e), keeping the fifth ($\omega_e x_e$) as an internal check. It is unfortunately true that the conclusions of the present study were based on a very limited set of experimental data, but we feel that a larger number would have, if anything, enhanced our confidence in them.

	HI	HBr	HCl	HF	BBr	BCl	BF	AlBr
α	2.1438	2.1438	2.1438	2.2214	2.0017	2.0017	1.7583	1.3948
β	− 4.2458	− 4.2458	− 4.2458	0.0000	− 9.6711	− 9.6711	0.0000	− 3.4286
γ	3.2936	3.5832	3.3118	0.0000	2.5099	2.3299	0.0000	1.4473
% error in α_e	0.0	0.0	0.0	−16.3	0.0	0.0	−28.7	0.0
% error in $\omega_e x_e$	20.1	17.4	12.2	− 2.4	−18.8	− 2.9	− 34.1	9.9

Table IV. The calculated molecular parameters of the studied halides.

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[17] These are: (i) $V''(r_e) = 2\alpha^2 D_e + 2\beta$, (ii) $V'''(r_e) = -6\,[\alpha^3 D_e + \beta\gamma]$, and (iii) $V^{\text{iv}}(r_e) = 14\,\alpha^4 D_e + 12\,\beta\,\gamma^2$.