

# Derivation of force constants based on the electric field gradient

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## ABSTRACT

The present work devotes to studying the electric properties: electric quadrupole moment and electric field gradient (EFG) of molecules PdH and (PdH)<sup>-2</sup> based on the full relativistic theory. It is the first time to explore that the force constants are essentially caused by electric field gradients, and indirectly with spectroscopic data. If EFG is positive, zero or negative, then the  $k_2$  will be positive, zero or negative. Therefore, second order force constants are adjustable to changing the intensity of EFG.

**Keywords:** Full Relativistic Quantum Mechanical Theory; Electric Quadrupole Moment; Electric Field

## 1. INTRODUCTION

The force constants of diatomic molecules, in general, are derived from spectroscopic data [1], or may be determined by a least-square fitting to the data of quantum mechanic calculations [2], and the latter is time tediously consuming and complicated. If the force constants and dissociation energy are known, the calculations of diatomic potential are numerically straightforward.

It is explored that the force constants are essentially connected with the electric field gradient (EFG), and indirectly with spectroscopic data. There are some works for the calculations of the electric field gradient using non-relativistic or relativistic quantum mechanic [3-5]. The present work has evaluated the EFG of molecules PdH and (PdH)<sup>-2</sup> based on the full relativistic quantum mechanic.

## 2. THE FULL RELATIVISTIC THEORY

Symmetry plays an important role for quantum mechanical theory. There are three levels for quantum me-

chanical method: Non-relativistic based on the single point group, relativistic based on the double group [6,7] and relativistic based on the full symmetry group or quaternion symmetry [8,9].

In consideration of the equivalence of space and time, for the relativistic theory based on the full symmetry group or quaternion symmetry, the time reversal symmetry operation is included in the symmetry group. It is well known that the product of two space symmetry operators is represented by the product of the corresponding unitary matrices in the theory of group representation, however, time reversal symmetry operation is an anti-unitary operator. The inclusion both of space and time operations, the group is called the full symmetry group, and their group representation is called a co-representation, this nomenclature is introduced by Wigner [8,9]. The co-representation is not unitary representation; however, it is still possible to be broken down to irreducible form. The third level, *i.e.*, relativistic quantum mechanical theory based on the full symmetry group or quaternion symmetry is applied by the work of T. Saue and the others.

Time reversal operator or called Kramer operator [7, 10,11] is defined as follows

$$\hat{K}\psi(r,t) = \psi^*(r,-t) \quad (1)$$

If Hamiltonian  $\hat{H}$  is a real function of  $r$ , then

$$\begin{aligned} \hat{K}\hat{H}(r)\psi(r,t) &= \hat{H}^*(r)\psi^*(r,-t) = \hat{H}(r)\psi^*(r,-t) \\ &= \hat{H}\hat{K}\psi(r,t) \end{aligned} \quad (2)$$

*i.e.*

$$[\hat{H}, \hat{K}] = 0 \quad (3)$$

The commutator (3) is the necessary and sufficient condition for two operators  $\hat{K}$  and  $\hat{H}$  having the same set of eigenfunctions, that is, the state is invariant to time reversal (motion reversal).

It is proved that time reversal operator is antiunitary [10,11], *i.e.*

$$\langle \hat{K}\psi | \hat{K}\phi \rangle = \langle \psi | \phi \rangle^* = \langle \phi | \psi \rangle \quad (4)$$

It is also anti-linear operator.

Kramer theorem [7,8,10,11]: It can be proved that  $\hat{K}^2 = -I$  corresponding to J value of half odd integer, *i.e.* fermions, there will be the new double degeneracy by time reversal; and  $\hat{K}^2 = +I$  corresponding to J value of integer, *i.e.* bosons, there will be no double degeneracy, where I identity.

For the time-independent Dirac equation

$$\hat{h}_D \psi = E \psi \quad (5)$$

where  $\hat{h}_D = \beta' mc^2 + c(\alpha \cdot \hat{p}) + \hat{V}$

$$\text{where, } \alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}; \beta' = \begin{bmatrix} 0 & 0 \\ 0 & 2I_2 \end{bmatrix}; \quad (6)$$

$I_2$  —  $2 \times 2$  Unit matrix.

And Pauli spins matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (7)$$

If  $\hat{V} = 0$ , it is the Dirac equation of free electrons.

Now, time reversal operator is defined using another equivalent method, *i.e.* Kramer theorem [8,9], in which  $\hat{K}^2 = -I$ , that is  $\hat{K}^2 \varphi = -\varphi = \bar{\varphi}$ , in which the state are recovered by twice of time reversal, however, the wave function is changed to the negative; If  $\hat{K}^2 = +I$ , that is  $\hat{K}^2 \varphi = \varphi$ , in which the state are recovered by twice of time reversal, the wave function is unchanged. Then  $\varphi$  and  $\bar{\varphi}$  are said to form a Kramers pair. Therefore, the operator can be expanded in terms of Kramer's partners  $\{\varphi\}$  and  $\{\bar{\varphi}\}$ . For example, Hermitian of one-electron operator [8,9] is defined as follows

$$\hat{h}_D = \begin{pmatrix} A & B \\ -B^* & A^* \end{pmatrix} = \begin{pmatrix} \hat{V} & -ic\hat{d}_z & 0 & -ic\hat{d}_- \\ -ic\hat{d}_z & -2mc^2 + \hat{V} & -ic\hat{d}_- & 0 \\ 0 & -ic\hat{d}_+ & \hat{V} & ic\hat{d}_z \\ -ic\hat{d}_+ & 0 & ic\hat{d}_z & -2mc^2 + \hat{V} \end{pmatrix} \quad (8)$$

where

$$\hat{d}_z = \frac{\partial}{\partial z}, \hat{d}_\pm = \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y}. \quad (9)$$

It is easy to know

$$A = \begin{pmatrix} \hat{V} & -ic\hat{d}_z \\ -ic\hat{d}_z & -2mc^2 + \hat{V} \end{pmatrix} = A^+ \quad (10)$$

$$B = \begin{pmatrix} 0 & -ic\hat{d}_- \\ -ic\hat{d}_- & 0 \end{pmatrix} = -B^+ = \begin{pmatrix} 0 & -ic\hat{d}_+ \\ -ic\hat{d}_+ & 0 \end{pmatrix} \quad (11)$$

That is, A is a Hermitian and B is antihermitian. For Kramer's partners, Dirac operator  $\hat{h}_D$  can be expressed as

$$\hat{h}_D = I_2 \otimes \begin{pmatrix} \hat{V} & 0 \\ 0 & -2mc^2 + \hat{V} \end{pmatrix} - c \check{i} \otimes \begin{pmatrix} 0 & \hat{d}_z \\ \hat{d}_z & 0 \end{pmatrix} - c \check{j} \otimes \begin{pmatrix} 0 & \hat{d}_y \\ \hat{d}_y & 0 \end{pmatrix} - c \check{k} \otimes \begin{pmatrix} 0 & \hat{d}_x \\ \hat{d}_x & 0 \end{pmatrix} \quad (12)$$

where,  $\hat{h}_D$  is expressed as the quaternion, which exhibits the time reversal symmetry.

Quaternion algebra [12] was developed by Hamilton and Fresenius, however, limited applications of quaternion in quantum mechanics have been made in recent years.

Quaternion is expressed as

$$q = \sum_{\lambda=0}^3 V_\lambda e_\lambda = V_0 + V_1 \check{i} + V_2 \check{j} + V_3 \check{k} \quad (13)$$

where

$$e_1 = \check{i} \leftrightarrow i\sigma_z; e_2 = \check{j} \leftrightarrow i\sigma_y; e_3 = \check{k} \leftrightarrow i\sigma_x \quad (14)$$

where  $\check{i}, \check{j}, \check{k}$  are quaternion units, *i*-imaginary,  $V_0, V_1, V_2$  and  $V_3$  are real part,  $\sigma_x, \sigma_y$  and  $\sigma_z$  are Pauli spins matrices in (7). Quaternion includes 3-dimension complex space and one dimension real space. It is known from (7) to (11) that quaternion algebra includes both time and space reversal symmetry, then, it is called the full symmetry group, its matrix representation is called co-representation. The  $\hat{h}_D$  in (12) is the Dirac operator of full symmetry group. The Dirac equation can therefore be rewritten into quaternion algebra form

$${}^q \hat{h}_D {}^q \psi = E {}^q \psi \quad (15)$$

### 3. THE CALCULATIONS OF ELECTRIC PROPERTIES

The calculations of energy and electric properties: electric quadrupole moment, electric field gradients of molecules PdH based on the full relativistic quantum mechanical theory with the basis dyall.v2z using of program DIRAC10. The results are shown as **Tables 1** and **2**.

The charge distributions of dipole for molecule PdH is calculated as follows

$$q = \frac{\mu}{r} = \pm \frac{3.37730}{1.52859} = \frac{3.37730 \times 10^{-18} \text{ (CGSE} \cdot \text{cm)}}{1.52859 \times 10^{-8} \text{ (cm)} \times 3 \times 10^9} = \pm 0.73647 / 10^{-19} \text{ C}$$

**Table 1.** The energy, electric dipole and quadrupole moment of molecule PdH.

Electron number*	47
PdH	
Bond distance/Å <sup>0</sup>	1.52859
E/au	-5044.9894383303208
Electric dipole/Debye	3.37730
Electric quadrupole/a.u.	$Q_{xx} = -4.916192952229$
	$Q_{yy} = -4.916192952229$
	$Q_{zz} = 9.832385904457$

\*Electron number 46 for Pd and 1 for H.

**Table 2.** The electric field gradients (EFG),  $k_2$  and  $\omega$  for molecules.

Molecule	PdH	(PdH) <sup>-2</sup>
(EFG/au)*	Nucleus: pd	Nucleus: pd
	$q_{xx} = q_{yy} = -1.029691$	$q_{xx} = q_{yy} = 0.01756005$
	$q_{zz} = 2.059396$	$q_{zz} = -0.03512008$
	Nucleus: H	Nucleus: H
	$q_{xx} = q_{yy} = -0.0924681$	$q_{xx} = q_{yy} = -0.0789845$
	$q_{zz} = 0.184936$	$q_{zz} = 0.157969$
$k_2/10^6$ (ergcm <sup>-2</sup> )	0.598662	0.197680
$\omega/\text{cm}^{-1}$	3187.5 (PdH)	1831.6 (PdH)
	2264.97 (Pd <sup>2</sup> H = PdD)	1301.5 (Pd <sup>2</sup> H = PdD)

PdH: Electron number 46 for Pd and 1 for H; (PdH)<sup>-2</sup>: Electron number 48 for Pd and 1 for H; \*1 a.u. = 9.71736E + 21 Vm<sup>-2</sup>.

However, its quadrupole is the second-rank tensor with two dimension charge distribution (vertical plane  $\sigma_V$ ), **Figure 1** in which the unit of charge distributions is 10<sup>-19</sup> C, C-coulomb,

The  $q_{zz}$  and  $q_{xx(y)}$  of PdH can be calculated as

$$\begin{aligned} q_{zz} &= \frac{Q_{zz}}{r} = + \frac{9.8338590}{1.52859} \\ &= + \frac{9.83238590 \times 10^{-18} \text{ (CGSE} \cdot \text{cm)}}{1.528590 \times 10^{-8} \text{ (cm)} \times 3 \times 10^9} \\ &= +2.144107 / 10^{-19} \text{ C} \end{aligned}$$

$$\begin{aligned} k_2 &= 1 \text{ au (charge)} \times 1 \text{ au (EFG)} = -4.8029 \times 10^{-10} \text{ (CGSE)} \times 9.71736 \times 10^{21} \frac{\text{V}}{\text{m}^2} \\ &= -4.8029 \times 10^{-10} \text{ (CGSE)} \times 9.71736 \times 10^{21} \times \frac{\text{V}}{10^4 \text{ cm}} \times \frac{1}{300} \text{ (CGSE)} \frac{1}{\text{cm}} \\ &= 1.55717 \times 10^6 \frac{\text{dyne}}{\text{cm}} = 1.55717 \times 10^6 \text{ (g} \cdot \text{sec}^{-2}) = 1.55717 \times 10^6 \frac{\text{g} \cdot \text{cm}^2 \cdot \text{sec}^{-2}}{\text{cm}^2} \\ &= 1.55717 \times 10^6 \frac{\text{g} \cdot \text{cm} \cdot \text{sec}^{-2}}{\text{cm}} \left( \frac{\text{dyne}}{\text{cm}} \right) = 1.55717 \times 10^6 \left( \frac{\text{erg}}{\text{cm}^2} \right) \end{aligned} \quad (20)$$

For neutral molecule PdH, *i.e.*, electron number of 47, and the  $q_{zz} = 2.059396$  for Pd and  $q_{zz} = 0.184936$

$$\begin{aligned} q_{xx(y)} &= \frac{Q_{xx(y)}}{r} = - \frac{4.9161929}{1.52859} \\ &= - \frac{4.9161929 \times 10^{-18} \text{ (CGSE} \cdot \text{cm)}}{1.52859 \times 10^{-8} \text{ (cm)} \times 3 \times 10^9} \\ &= -1.0721 / 10^{-19} \text{ C} \end{aligned}$$

Suppose the potential of diatomic can be expressed as

$$V = \frac{1}{2} k_2 (r - r_e)^2 + \frac{1}{6} k_3 (r - r_e)^3 + \frac{1}{24} k_4 (r - r_e)^4 \quad (16)$$

Where  $r$  is the nuclear distance and  $r_e$  is its equilibrium nuclear distance, and  $k_2$ ,  $k_3$  and  $k_4$  are the quadratic, cubic and quartic force constants, respectively. The negative derivative of potential with respect to bond distance  $r$  is the electric field force of nuclei, therefore

$$qE = f = - \frac{\partial V}{\partial r} = -k_2 (r - r_e) - \frac{1}{2} k_3 (r - r_e)^2 - \frac{1}{6} k_4 (r - r_e)^3 \quad (17)$$

where  $E$  is the electric field strength,  $q$  is the electric charge.

From (17), it leads to the electric field gradient  $\frac{\partial E}{\partial r}$  (EFG)

$$q \frac{\partial E}{\partial r} = -k_2 - k_3 (r - r_e) - \frac{1}{2} k_4 (r - r_e)^2 \quad (18)$$

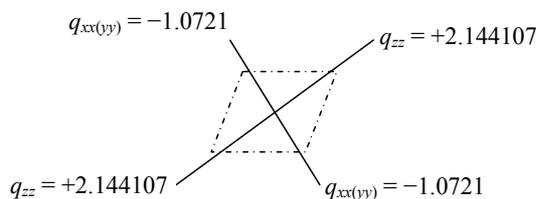
If  $r = r_e$ , then, the quadratic force constant  $k_2$  will be

$$q \frac{\partial E}{\partial r} = k_2 \quad (19)$$

where  $q$  is negative and take its absolute value. If EFG is positive, zero or negative, then, the  $k_2$  will be positive, zero or negative. If we want the  $k_2$  to be zero or negative, it is possible to make the EFG descended or tend to negative.

Suppose there is 1 au of electric charge and at 1au of electric field gradient, the quadratic force constant  $k_2$

for H, and their Mulliken Atomic Charges: Pd = 0.037613, H = -0.037613. Then



**Figure 1.** The quadrupole charge distribution of PdH.

$$k_2 = \left[ \frac{2.059396}{9.962387} + \frac{0.184936}{1.037613} \right] \times 1.55517 \times 10^6 \text{ (erg} \cdot \text{cm}^{-2})$$

$$= 0.598662 \times 10^6 \text{ (dyne/cm)}$$

And Harmonic frequencies

$$\omega = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} = \frac{1}{2 \times 3.1416 \times 3 \times 10^{10}} \left( \frac{0.598662 \times 10^6 \times 6.023 \times 10^{23}}{0.99832471} \right)^{1/2}$$

$$= 0.0318750 \times 10^5 = 3187.50 \text{ cm}^{-1} \text{ for PdH}$$

$$\omega = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} = \frac{1}{2 \times 3.1416 \times 3 \times 10^{10}} \left( \frac{0.598662 \times 10^6 \times 6.023 \times 10^{23}}{1.97719645} \right)^{1/2}$$

$$= 0.02264968 \times 10^5 = 2264.968 \text{ cm}^{-1} \text{ for Pd}^2\text{H i.e. PdD}$$

where 1.97719645 is the reduced mass of PdD.

For (PdH)<sup>-2</sup>, *i.e.*, Electron number of 49, *i.e.*, and the  $q_{zz} = -0.03512008$  for Pd and  $q_{zz} = 0.157969$  for H,

and their Mulliken Atomic Charges: Pd = -1.785709, H = -0.214291. Then

$$k_2 = \left[ \frac{-0.03512008}{11.785709} + \frac{0.157969}{1.214291} \right] \times 1.55517 \times 10^6 \text{ (erg} \cdot \text{cm}^{-2})$$

$$= 0.197680 \times 10^6 \text{ (dyne/cm)}$$

And Harmonic frequencies

$$\omega = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} = \frac{1}{2 \times 3.1416 \times 3 \times 10^{10}} \left( \frac{0.19768024 \times 10^6 \times 6.02 \times 10^{23}}{0.99832471} \right)^{1/2}$$

$$= 0.0183164 \times 10^5 = 1831.64 \text{ cm}^{-1} \text{ for PdH}$$

$$\omega = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} = \frac{1}{2 \times 3.1416 \times 3 \times 10^{10}} \left( \frac{0.19768024720 \times 10^6 \times 6.02 \times 10^{23}}{1.97719645} \right)^{1/2}$$

$$= 0.0130153 \times 10^5 = 1301.53 \text{ cm}^{-1} \text{ for Pd}^2\text{H i.e. PdD}$$

where 1.97719645 is the reduced mass of PdD.

All the electric field gradients (EFG), quadratic force constants  $k_2$  and Harmonic frequencies  $\omega$  for molecules are listed in **Table 2**.

#### 4. CONCLUSIONS

From Equation (19), it is proved that the second order force constant is directly derived from electric field gradients EFG. Therefore, it is the first time to explore that the force constant is essentially caused by electric field gradients, and the second order force constant and its harmonic oscillator frequency have been derived from electric field gradients. However, the force constants are usually derived from spectroscopic data; however, it is indirect with spectroscopic data. Therefore, this is the sup-

plemental to the spectral values.

Momentously, the second order force constants are adjustable to changing the intensity of EFG. If EFG is positive, zero or negative, then, the  $k_2$  will be positive, zero or negative. It is obvious to see from **Table 2** that  $k_2$  is descended from  $0.59866 \times 10^6 \text{ erg} \cdot \text{cm}^{-2}$  of PdH down to  $0.19768 \times 10^6 \text{ erg} \cdot \text{cm}^{-2}$  of (PdH)<sup>-2</sup>, where, it's EFG from  $q_{zz} = 0.184936$  that is down to  $q_{zz} = 0.157969$ .

The linear charge distributions,  $\pm 0.73647/10^{-19} \text{ C}$ , of dipole moment for molecule PdH is much less than its two-dimension charge distribution of quadrupole moment  $q_{zz} = 2.144107/10^{-19} \text{ C}$  and  $q_{xx(yy)} = -1.0721/10^{-19} \text{ C}$ . The charge distribution of PdH could be comparable with that of molecules HBr or HCl; however, it does not like HF, to see **Table 3** of references [13], and therefore quadrupole

**Table 3.** The linear charge distributions of molecule (HX, X = F, Cl, Br) [13].

	HF/ $10^{-19}$ C	HCl/ $10^{-19}$ C	HBr/ $10^{-19}$ C
Dipole moment	$\pm 0.6986$	$\pm 0.310468$	$\pm 0.2096$
Quadrupole moment			
$q_{zz}$	+0.4128	+0.7641	+0.9291
$q_{xx(yy)}$	-0.2063	-0.3821	-0.4645

charge distributions are quite characteristic for electric properties.

## REFERENCES

- [1] Huber, K.P. and Herzberg, G. (1979) Molecular spectra and molecular structure I-IV, Van Nostrand Reinhold Company.
- [2] Murrell, J.N. (1984) Molecular potential energy functions. John Wiley, New York.
- [3] Neese, F., Wolf, A., Fleig, T., Reiher, M. and Hess, B.A. (2005) Calculation of electric-field gradients based on higher-order generalized Douglas-Kroll-Hess transformations. *Journal of Chemical Physics*, **122**, 204107-204117. <http://dx.doi.org/10.1063/1.1904589>
- [4] Visscher, L., Enevoldsen, T., Saue, T. and Oddershede, J. (1998) Molecular relativistic calculations of the electric field gradients at the nuclei in the hydrogen halides. *Journal of Chemical Physics*, **109**, 9677-9684. <http://dx.doi.org/10.1063/1.477637>
- [5] Mastalerz, R., Barone, G., Lindh, R. and Reiher, M. (2007) Analytic high-order Douglas-Kroll-Hess electric field gradients. *Journal of Chemical Physics*, **127**, 074105-047117. <http://dx.doi.org/10.1063/1.2761880>
- [6] Luding, W. and Falter, C. (1996) Symmetries in physics. Springer-Verlag Heidelberg, Berlin.
- [7] Tinkham, M. (1964) Group theory and quantum mechanics. McGraw-Hill, New York.
- [8] Saue, T. and Jensen, H.J.A. (1999) Quaternion symmetry in relativistic molecular calculations. *Journal of Chemical Physics*, **111**, 6211-6222. <http://dx.doi.org/10.1063/1.479958>
- [9] Saue, T. and Jensen, H.J.A. (2003) Linear response at the 4-components relativistic level. *Journal of Chemical Physics*, **118**, 522-536.
- [10] Zhu, Z.H. (1996, 2007) Atomic and molecular reaction statics. Science Press, Beijing.
- [11] Zhu, Z.H. (2007) The atomic and molecular reaction statics. *Science in China Series G: Physics Mechanics and Astronomy*, **50**, 581-590. <http://dx.doi.org/10.1007/s11433-007-0054-6>
- [12] Charlie, H. (1976) Introduction to mathematical physics. Prentice Hall, Inc., Englewood Cliffs.
- [13] Zhu, Z.H., Meng, D.Q., Tang, Y.J. and Wan, M.J. (2012) Electric properties of molecules (HX, X = F, Cl, Br) based on the full relativistic theory. *Science in China Series G: Physics Mechanics and Astronomy*, **42**, 392-399.