Chapter 12
Quantum Chemistry at the High Pressures: The eXtreme Pressure Polarizable Continuum Model (XP-PCM)

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Abstract In this chapter, we review some recent developments in our XP-PCM method to introduce the effect of high pressure ($p > 1$ GPa) in the quantum chemistry study of molecular properties and processes. After a presentation of the physical basis and the computational aspects of the XP-PCM model, we give examples of its recent applications. These applications regard the study and analysis of the electron distribution, of the equilibrium geometry, and of the vibrational frequencies of molecular systems under high pressure.

Keywords DFT · Equilibrium geometry · Vibrational frequencies · Pressure effects · eXtreme-pressure polarizable continuum model

12.1 Introduction

In this chapter, we present a short review of our model in title, aimed to introduce the effects of high pressure (larger than 1 GPa) in the quantum chemical description of molecular systems. The issue of high pressure in the quantum mechanical calculation for atoms and molecules has a long history, which dates back to 1937 [1]. However, this history testimonies of models which have been restricted, so far, to the study of very simple systems as atoms or diatomic molecules, remaining excluded by the impressive developments in the modern computational quantum chemistry.

As denoted by its name, the XP-PCM model is a generalization of the well-known polarizable continuum model for the study of molecular properties and processes in solution at standard conditions of pressure and temperature [2, 3]. A first version of the XP-PCM was presented in 2008 [4]. More developed versions have been presented for applications to the study of the effect of extreme high pressures on the equilibrium geometries and vibrational frequencies of molecular systems [5–7]. The method has recently been extended to study the effect of extreme pressure on the

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electronic excitations of molecular systems [8], and to the study of potential energy surfaces for chemical reactions at extreme high pressure [9].

In its basic version, the XP-PCM model describes molecular systems (the solute) in a dense medium at extreme high pressure ($p > 1\,\text{GPa} = 10^5$ bar). The medium is represented as a continuum material distribution having a void molecular cavity in which the molecular solute is accommodated. The continuum material is characterized in terms of its dielectric permittivity and its averaged electronic charge distribution, at the given condition of pressure. The molecular solute is described at the quantum mechanical level, and hence its electron distribution spreads in the medium outside the void cavity, where it overlaps with the electron distribution of the medium. Pressure enters through the Pauli repulsive interaction originating by this overlap, and the effects of the pressure are modeled by shrinking the volume of the molecular cavity. The shrinking of the cavity increases the amount the electronic charge density of the molecular solute that lies outside of the cavity boundary, with a consequent increase of the Pauli repulsion with the solvent.

The present contribution is organized as follows: After a presentation of the essential of the computational aspects of the XP-PCM model for the study of the molecular systems at extreme pressure (Sect. 12.2), we give examples of its numerical applications to the studies of the effect of the pressure on the electron distribution (Sect. 12.3), of the effect of the pressure on the equilibrium geometry (Sect. 12.4), and of the effect of the pressure on the vibrational frequencies (Sect. 12.5). Finally, in Sect. 12.6, we draw some provisional concluding remarks on the XP-PCM model.

12.2 The Essential of the XP-PCM Method for Molecules Under High Pressure

In this section, we summarize the basic XP-PCM equations for the quantum mechanical description of a molecular the solute in a dense medium at extreme high pressure.

The molecular system is described, in the usual clamped nuclei approximation, by an effective electronic Hamiltonian which may be written as

$$\hat{H} = \hat{H}^o + \hat{V}_e(\Psi) + \hat{V}_r \tag{12.1}$$

where H^o the electronic Hamiltonian of the isolated molecule; $\hat{V}_e(\Psi)$ represents the solute–solvent electrostatic interaction, giving origin to the solvent reaction field of the PCM model, and depending on the electronic wave-function $|\Psi>$ of the molecule [2]; The operator $\hat{V}_r$ represents the exchange–repulsion (Pauli) interaction of the molecular solute with a statistical average distribution of the surrounding molecules of the external medium. According to the theory of intermolecular interaction [10], the exchange–repulsion contribution originates from the overlap between the electronic distribution of the molecular solute and a mean electronic distribution of the solvent (i.e., the external medium). The mean electronic distribution of the solvent is approximated as a uniform distribution outside of the cavity hosting the molecular solute, and with zero density inside the cavity. As a consequence, only the portion of the electronic distribution of the molecular solute lying outside the cavity overlaps with the uniform electronic distribution of the solvent, determining the solute–solvent Pauli repulsion.

The Pauli repulsion operator V_r corresponds to a repulsive step potential barrier located at the boundary of the cavity hosting the molecular solute [10][1]:

$$\hat{V}_r = \int \hat{\rho}(\mathbf{r})\mathscr{V}_0\Theta(\mathbf{r})d\mathbf{r} \tag{12.2}$$

$\hat{\rho}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$ is the electron density operator (over the N electrons of the molecular system), and $\mathscr{V}_0$ is the height of a barrier potential $\Theta(\mathbf{r})$ located at the boundary of the cavity $\mathbf{C}$:

$$\Theta(\mathbf{r}) = \begin{cases} 1 \ \mathbf{r} \subseteq \mathbf{C} \\ 0 \ \mathbf{r} \nsubseteq \mathbf{C} \end{cases} \tag{12.3}$$

The potential barrier height V_0 is given by

$$\mathscr{V}_0(s) = \frac{\mathscr{V}_0}{s^{3+\eta}} \qquad s = \left(\frac{V_c}{V_c^0}\right)^{1/3} \tag{12.4}$$

where $\mathscr{V}_O$ is the step barrier at the standard condition of pressure [2], and V_c and V_c^0 are, respectively, the actual volume of the cavity and the volume corresponding to the standard condition of pressure. In Eq. (12.4), η is a semi-empirical parameter that gauges the strength of the solute-solvent Pauli repulsion [13].

The effective electronic Hamiltonian (12.1) implies a quantum mechanical energy functional, G_{e-r}, which is defined as:

$$G_{e-r} = <\Psi|\hat{H}^o + \frac{1}{2}\hat{V}_e(|\Psi>) + \hat{V}_r|\Psi> + \tilde{V}_{nn} \tag{12.5}$$

The energy functional (12.5) has the thermodynamic status of a free energy for the whole molecule-external medium system, with respect to a reference state given by the non-interacting electrons and nuclei of the molecular solute and by the unperturbed external medium having a preformed cavity to host the solute.[2]

The time-dependent Schrödinger equation for the effective Hamiltonian (12.1) determines the electronic wave-function $|\Psi>$ of the molecular system [14]:

$$[\hat{H}^o + \hat{V}_e(|\Psi>) + \hat{V}_r]|\Psi> = E|\Psi> \tag{12.6}$$

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[1] An alternative definition of the operator V_r has been recently given by Chipman and co-workers in terms of the gradients of the electron density operator [11, 12].

[2] The factor $1/2$ in front to the operator $\hat{V}_e(|\Psi>)$ is due to the nonlinear nature of this operator, and $\tilde{V}_{nn}$ is the nuclei–nuclei interaction contribution in the presence of the external medium.

The solution of this equation, which can be approached at the available approximation levels of the Computational Quantum Chemistry (HF/DFT, Couple-Cluster, …), gives access to the properties of the molecular systems under extreme pressure, at these various levels of theory. Within the XP-PCM model, as for the standard PCM model, the electronic response properties of the molecular solute can be expressed as derivatives of the free-energy functional G_{e-r} with respect to suitable internal or external perturbations. This connection between the molecular properties and the free-energy functional G_{e-r} is a consequence of the form that the Hellmann–Feynman theorem [15, 16] takes for the PCM model [3, 17].

The free-energy functional G_{e-r} may also act as the Born–Oppenheimer potential energy surfaces ruling the nuclear motion of the solute, if a rigid geometry of the cavity hosting the molecular solute is assumed. This approximation can be used the case of molecules whose equilibrium geometry do not involve large displacements of the nuclei under the effect of extreme pressure. This approximation has been used in all the applications presented in this chapter. In the case of molecular processes involving large amplitude motions of the nuclei, as in the conformational changes, or along an intrinsic reaction path, the potential energy surfaces ruling the nuclear motion is obtained by adding to the electronic free-energy functional G_{e-r} a free-energy contribution due to the variation of the cavity geometry within the molecular process.

The free-energy functional G_{e-r} may also act as the Born–Oppenheimer potential energy surfaces ruling the nuclear motion of the solute, if a rigid geometry of the cavity hosting the molecular solute is assumed. This approximation of a rigid cavity may be used the case of molecules whose equilibrium geometry do not involve large displacements nuclei under the effect of extreme pressure. This approximation has been used in the applications presented in this chapter. On the contrary, in the case of molecular processes involving large amplitude motions of the nuclei, as in the conformational changes, or along intrinsic reaction paths, the effective potential energy surfaces ruling the nuclear motion are obtained by adding to the electronic free-energy functional G_{e-r} a free-energy contribution due to the variation of the cavity geometry within the molecular process [9].

In the XP-PCM method, the pressure is not an input parameter, and it is defined in terms of the dependence of the electronic free-energy functional G_{e-r} with respect to the volume of the cavity hosting the molecular solute:

$$p = -\left(\frac{\partial G_{e-r}}{\partial V_c}\right) \tag{12.7}$$

where V_c is the volume of the cavity.

The cavity of the molecular solute is defined as the envelope of spheres centered on the solute atomic nuclei. The radii of these atomic spheres are given by the product of the corresponding van der Waals radii [18] times a uniform scaling factor, f. To increase the pressure, the volume of the cavity V_c is decreased by reducing the value

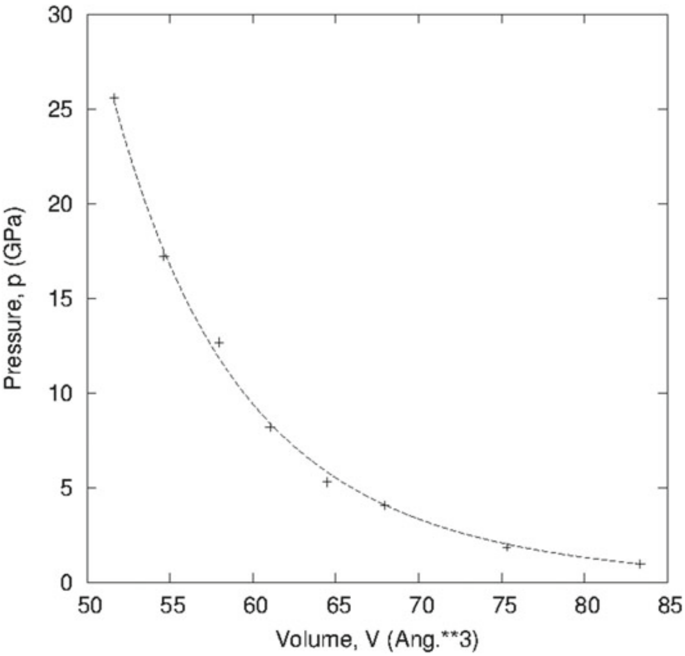

Fig. 12.1 XP-PCM results for the pressure, p, as a function of the cavity volume, V_c, for the case of diborane as molecular solute. See Ref. [5] for computational details

of the scaling factor f with respect the reference value $f_0 = 1.2$. Figure 12.1 shows the pressure as a function of the volume of the cavity for the case of the diborane molecule [5].

12.3 Effect of the Pressure on the Electron Density Distribution

Let us consider a molecular solute at a given fixed geometry in a dense phase at extreme pressure. Under this condition, the effect of the pressure on the molecular properties reflects the increase of the Pauli repulsion operator, V_r, in the effective electronic Hamiltonian (12.1). In fact, as we have described previously, XP-PCM models the effect of the pressure by reducing the volume of the cavity hosting the molecular solute, with a corresponding increase of the solute–solvent Pauli repulsion. The molecular system reacts to this perturbation rearranging its electronic wave-function, to which corresponds a change of the related electronic properties. As an example of the effect of the pressure on the electronic properties, we consider the case of the one-electron density $\rho(\mathbf{r})$.

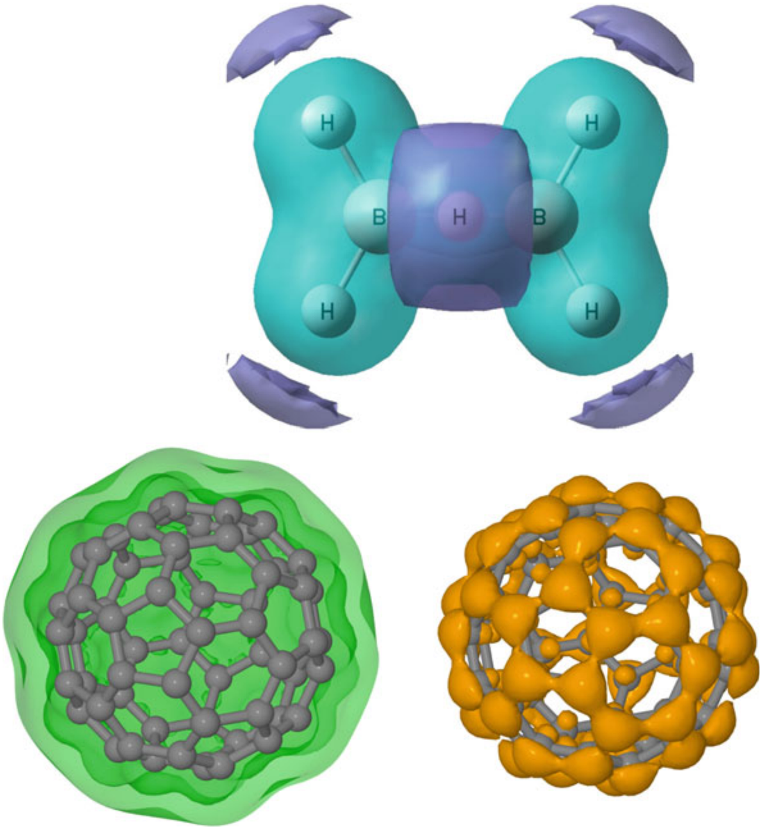

Fig. 12.2 XP-PCM iso-surfaces of the electron density differential $\Delta\rho(p) = \rho(p) - \rho(0)$ for diborane (*top*) and Buckminsterfullerene (*bottom*) under extreme pressure ($p = 1.0\,\mathrm{GPa}$). Diborane: *blue-violet* iso-surfaces correspond to a decrease of electron density $\Delta\rho < 0$ while aquamarine iso-surface corresponds to an increase of electron density $\Delta\rho > 0$; *C*60: *light-green* iso-surface corresponds to a decrease of electron density $\Delta\rho < 0$ while *orange* iso-surface corresponds to an increase of electron density $\Delta\rho > 0$

Figure 12.2 shows the differential of the electron density ($\Delta\rho(p) = \rho(p) - \rho(0)$) induced by the pressure p for diborane [5] and Buckminsterfullerene (C60) [6]. The effect of the pressure corresponds to a flux of electrons from outer regions of the molecular systems toward more internal regions. In particular, the increase of the $\rho(\mathbf{r})$ is concentrated in the internuclear regions of these molecular systems. The differential of the electron density $\Delta\rho(p)$ can be expressed in terms of the mixing between the molecular orbital (MO) induced by the pressure. At the first order, we can write:

$$\Delta\rho(p) = 2\sum_{i}^{occ} \phi_i^0 \phi_i^{(1)} \tag{12.8}$$

where the summation is over the occupied MO, ϕ_i^0 are the unperturbed MO and $\phi_i^{(1)}$ are the first-order perturbations induced by the one-electron Pauli perturbation v_r.[3] In an uncoupled MO perturbation scheme,[4] $\phi_i^{(1)}$ is given by

$$\phi_i^{(1)} = \sum_a^{vac} < \phi_i^0|v_r|\phi_a^0 > /(\varepsilon_i^0 - \varepsilon_a^0) \tag{12.9}$$

where the summation runs over the vacant MO $\phi_a^0 >$ and $(\varepsilon_i^0 - \varepsilon_a^0)$ are orbital energy differences.

The Pauli repulsion operator v_r is totally symmetric with respect to the symmetry point group of the molecular system (the pressure acts isotropically), hence reasons of symmetry restrict the summation over the vacant MO that span the same symmetry (irreducible representation) of the occupied MO ϕ_i^0. Therefore, each term of Eq. (12.8) is totally symmetric, and so the difference of the electron density $\Delta\rho(p)$, as clearly shown in Fig. 12.2.

As we will see in the next Section, the differential of the electron density ($\Delta\rho(p) = \rho(p) - \rho(0)$) plays a significant role in the discussion of the effect of the pressure on the equilibrium geometry.

12.4 Effect of the Pressure on Equilibrium Geometry

The XP-PCM method can study the evolution of the equilibrium geometry of molecular systems under extreme pressure. The equilibrium geometries are determined by exploiting very effective optimization processes, thanks to the available analytical form of the gradients of the electronic energy functional G_{e-r} [19]. In Fig. 12.3, we show the evolution of the variations of the bond lengths distances in diborane [5] and Buckminsterfullerene [6] as functions of the pressure, up to 20 GPa. For these molecular systems, all the atomic bond lengths are shortened with the increase of the pressure, with a linear dependence with respect to the pressure.

Is there an explanation of this linear behavior of the bond lengths with pressure? What is the physical origin of this response of the molecular geometry to the pressure? Both questions find a physically coherent explanation with the XP-PCM method.

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[3] Formally, the Pauli repulsion operator for N electrons of Eq. (12.2) may be written as $\hat{V}_r = \hat{v}_r(\mathbf{r})$ with $\hat{v}_r(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r'}_i)V_0\Theta(\mathbf{r})$.

[4] An uncoupled molecular orbital (MO) perturbation scheme is a perturbation method that evaluates the effect of the perturbation on the molecular orbital by neglecting the effects that the perturbation has on the electron–electron repulsion contribution of the Fock operator.

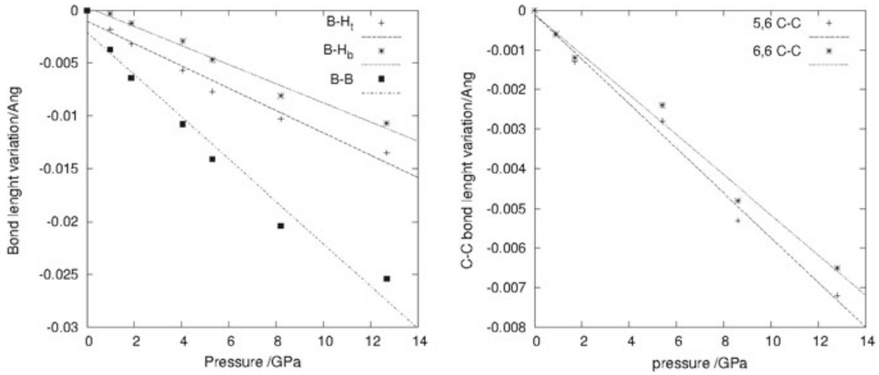

Fig. 12.3 XP-PCM bond lengths variations in diborane (*left panel*) and Buckminsterfullerene (*right panel*) as functions of the pressure. For diborane, B$-$H$_t$, B$-$H$_b$, B$-$B denote, respectively boron–hydrogen (terminal), boron–hydrogen (bridge), boron–boron bonds; for fullerene C60, 5,6C–C, 6,6C–C denote, respectively, the 5,6 and 6,6 carbon–carbon bonds. See Refs. [5, 6] for the computational details

12.4.1 On the Linear Dependence on Pressure of the Bond Distances

As said in Sect. 12.2, the potential energy function for the nuclei motion of the molecular system under an external pressure is given by the electronic energy G_{e-r}. Hence, the equilibrium geometry of the molecules corresponds to a minimum of the potential energy G_{e-r}. The potential energy G_{e-r}, may be formally expanded near the equilibrium geometry in the gas phase with respect to both the nuclear coordinates $\mathbf{Q}$ and the pressure p. If we express the nuclear coordinates in terms of the normal vibrational coordinates, $\mathbf{Q}_i$, of the isolated molecule, $G_{e-r}(\mathbf{Q},p)$ may be expressed up to second order as [5, 20]

$$G_{e-r}(\mathbf{Q},p) = G_{e-r}(0,p) + \frac{1}{2}\sum_i k_i Q_i^2 + p\sum_i^{TS} \Gamma_i Q_i \qquad (12.10)$$

where $G_{e-r}(0,p)$ denotes the electronic energy at the equilibrium geometry $\mathbf{Q} = 0$ at the pressure p, Q_i and $k_i = (\partial^2 G_{e-r}/\partial^2 Q_i)_{\mathbf{Q=0}}$ are the i-th normal mode and the corresponding harmonic force constant, and Γ_i is a pressure coupling defined as:

$$\Gamma_i = \left(\frac{\partial^2 G_{e-r}}{\partial p \partial Q_i}\right)_{\mathbf{Q=0}} = \left(\frac{\partial G_{e-r}^{Q_i}}{\partial p}\right)_{\mathbf{Q=0}} \qquad (12.11)$$

The coupling parameter Γ_i corresponds to a mixed second derivative of the basic XP-PCM energy. This coupling parameter has the physical meaning of a molecular response function which describes the response to the pressure of the component of energy gradients along the normal mode coordinates, $G_{e-r}^{Q_i} = \left(\frac{\partial G_{e-r}}{\partial Q_i}\right)_{\mathbf{Q=0}}$. For symmetry reasons (as the pressure is isotropic, the symmetry point group of the molecule is conserved), the summation of Eq. (12.10) runs only over the totally symmetric (TS) normal modes of the isolated molecules.

At a given pressure p, the new equilibrium geometry is then determined by the condition

$$\frac{\partial G_{e-r}(\mathbf{Q}, p)}{\partial Q_i} = p\Gamma_i + k_i Q_i^{eq} = 0 \tag{12.12}$$

which gives:

$$Q_i(p)^{eq} = -\frac{\Gamma_i}{k_i} p \qquad i \subseteq TS \tag{12.13}$$

Equation (12.13) shows that *the changes of the equilibrium geometry in the molecule occur with shifts along the totally symmetric normal coordinate Q_i, the shifts linearly depending on the external pressure p*. This conclusion is in agreement with the linear correlation shown in Fig. 12.2.

It is useful to rewrite Eq. (12.13) in the following form

$$Q_i(p)^{eq} = -\frac{G_{e-r}^{Q_i}(p)}{k_i} \qquad i \subseteq TS \tag{12.14}$$

where $G_{e-r}^{Q_i}(p) = \Gamma_i p$ is the force induced by the pressure along the normal mode. This form is similar to the analogous equation developed within the framework of the Bell theory [21] to study the deformation of a molecular system under an external mechanical force.[5]

We now turn to the explanation of the physical origin of the force $G_{e-r}^{Q_i}(p)$ induced by the pressure on the nuclei of the molecular solute.

12.4.2 On the Origin of Forces Induced by the Pressure on the Nuclei

The force $G_{e-r}^{Q_i}(p)$, of Eq. (12.14), induced by the pressure on the nuclei of the molecular solute is a consequence of the primary effects that the pressure has on the electronic charge distribution that we have discussed previously in Sect. 12.3.

In Sect. 12.3, we have shown that the pressure induces, via the solute–solvent Pauli repulsion V_0, a difference of electron density, $\Delta\rho(\mathbf{r}; p)$, which corresponds to a flux of electrons from the outer regions of the molecular solute to its inner, inter-

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[5] For reasons of space, we can no further discuss this connection between our XP-PCM theory with the Bell theory and its extensions.

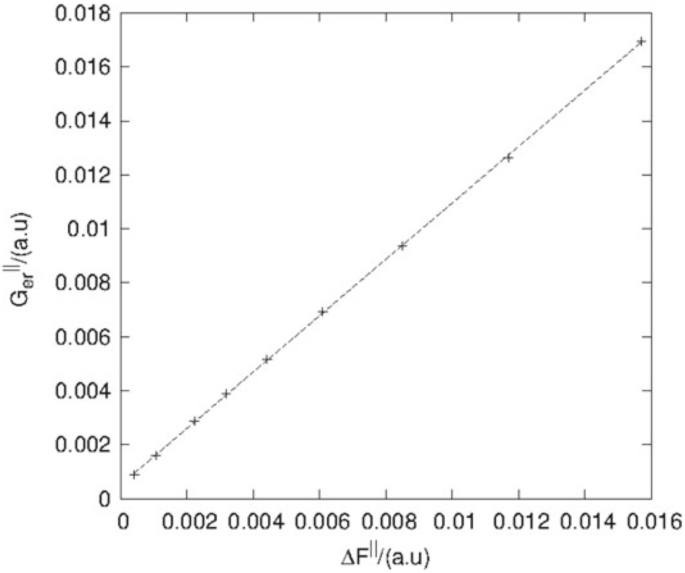

Fig. 12.4 Correlation between the XP-PCM analytical gradients of the energy $G_{er}^{||}$ and the Hellman–Feynman electrostatic forces in diborane. The *upper-script* || denotes a component along the direction of the boron–hydrogen (terminal) direction. All quantities are expressed in the pertinent atomic units (a.u) see Ref. [5] for computational details

atomic regions. The consequences of the differential of electron density may be analyzed by using the force concept based on the Hellmann–Feynman (*H–F*) electrostatic theorem [15, 16, 22–24]. According to this theorem, the force, $G_{e-r}^{Q_i}(p)$, induced by the pressure on the nuclei of the molecular solute is given by the electric field $\boldsymbol{\Delta F}(p)$ originated by the differential of electron density, $\Delta\rho(\mathbf{r};p)$:

$$\boldsymbol{\Delta F}(\mathbf{R}_A) = -Z_A \int \Delta\rho(\mathbf{r};p)\frac{(\mathbf{r}-\mathbf{R}_A)}{|\mathbf{r}-\mathbf{R}_A|^{3/2}}d\mathbf{r} = G_{e-r}^{\mathbf{R}_A} \tag{12.15}$$

where Z_A is the nuclear charge of A, and $\Delta\rho(\mathbf{r} : p)$.

A validation of the electrostatic origin of the force induced by the pressure on the nuclei is shown in Fig. 12.4, where the *H–F* electrostatic field of Eq. (12.15) at the terminal hydrogen atoms of diborane is compared with the corresponding energy gradient, $G_{e-r}^{\mathbf{R}_H}$, computed by analytical differentiation.

In this subsection, we have shown that the pressure has a direct effect on the electron density and that throughout this direct effect, pressure induces a further, indirect effect in molecular solute by changing its equilibrium geometry. This chain of effects triggered by the pressure does not stop here. In turn, the variation equilibrium geometry may influence, in general, many others molecular properties. In the following section, we will consider the case of the vibrational frequencies of a molecular solute under pressure.

12.5 Effect of the Pressure on the Vibrational Frequencies of Molecular Systems

The perspective of the theoretical modeling of the effects of the pressure on the vibrational frequencies is of considerable interest per se, as the theoretical results can be compared with available experimental data, toward a more robust validation of XP-PCM model. Furthermore, the XP-PCM model opens the way toward an understanding of the effects of the pressure on the vibrational frequencies, understanding that cannot be obtained by the experimental data alone.

Within the XP-PCM method, the vibrational frequencies (harmonic approximation) are computed at the equilibrium geometry corresponding to the given pressure (see the previous Sect. 12.4). The harmonic vibrational frequencies are determined from the Hessian matrix of the second derivatives of the electronic free-energy functional G_{er} with respect to the Cartesian coordinates of the nuclei. Here, we are assuming that during the vibrational displacements of the nuclei around the equilibrium geometry, the cavity hosting the molecular solute remains fixed. As already discussed in Sect. 12.2, only under this assumption, the electronic free-energy functional G_{e-r} acts as potential energy surface for the nuclei of the solute.

Specific physical arguments further motivate the approximation to held fixed cavity during the vibrational motion of the nuclei. Within the XP-PCM model, the vibrational frequencies of the molecules are evaluated taking into account the differences between the timescale of the vibrational degrees of freedom of the solvated molecule and the timescale of the various degrees of freedom (translational, rotational, vibrational, and electronic) of the molecules composing the solvent. The basic assumption is that the translational and rotational degrees of freedom of the solvent molecules remain fixed during a typical timescale of the vibrations of the molecular solute. On the other hand, the geometry of the cavity is correlated with the physical space non-accessible to the solvent molecules by the translational and rotational motion, and hence the displacements of the nuclei of the molecular solute around its equilibrium geometry are performed assuming a fixed geometry of the cavity.

12.5.1 On the Curvature *and* Relaxation *Effects of the Pressure on the Vibrational Frequencies*

In Fig. 12.5, we compare the XP-PCM linear coefficients of vibrational frequencies for Buckminsterfullerene ($d\nu/dp$) [6] with the available experimental counterpart. The figure collects both the radial and tangential normal modes of Buckminsterfullerene and shows that the correlation between the theoretical and experimental data is satisfactory. Similar results have been obtained for other molecular systems [5, 7].

The XP-PCM model allows to analyze these effects of the pressure on the vibrational frequencies in terms of two different physical mechanisms [5]. The first mechanism, called the *curvature* effect, is determined by the influence of the differential

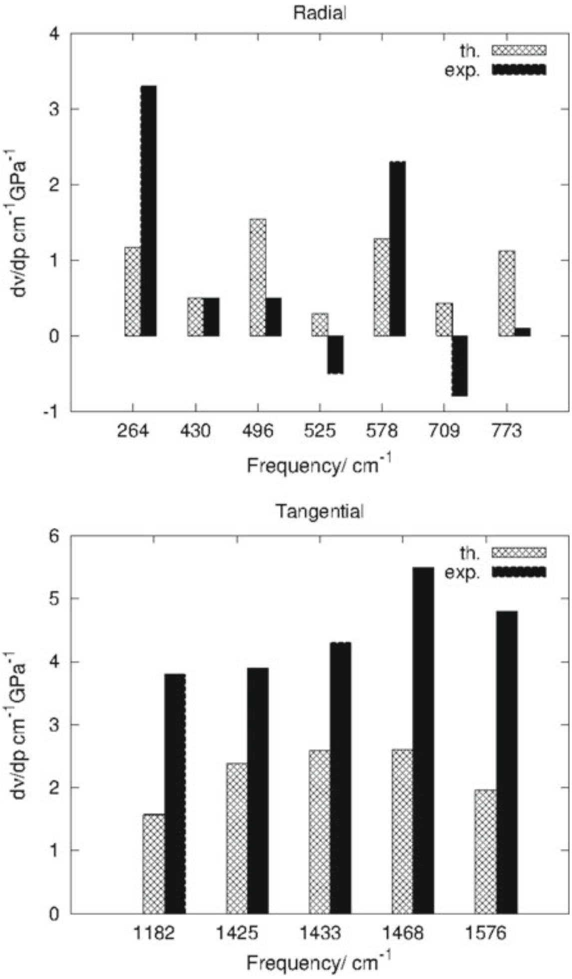

Fig. 12.5 XP-PCM study of the effect of the pressure on the vibrational frequencies (harmonic approximation) of Buckminsterfullerene: comparison between the computed linear pressure coefficients $(d\nu/dp)_{XP-PCM}$ (*blue bars*) and the available experimental data $(d\nu/dp)_{exp}$ (*green bars*). The *upper panel* is pertinent to the normal modes with displacements of the nuclei along direction normal to the molecular surface of C60. The *lower panel* is pertinent to the normal modes with displacements of the nuclei along directions tangential to the molecular surface of C60. See Ref. [6] for computational details

electron density induced by the pressure (see Sect. 12.3) on the harmonic force constant, evaluated at the equilibrium geometry in vacuo. This effect is determined as

$$\left.\frac{dk_i}{dp}\right|_{cur} = \left(\frac{\partial k_i}{\partial p}\right)_{\mathbf{Q}(0)} \tag{12.16}$$

and the corresponding *curvature* effect on the vibrational frequencies is denoted by $\left(\frac{\partial \nu(p)}{\partial p}\right)_{cur}$.

The second mechanism, called *relaxation* effect, is related to the influence that the shift of the equilibrium geometry induced by the pressure $\mathbf{Q}_i(p)$ has on the harmonic force constant:

$$\left.\frac{\partial k_i(p)}{\partial p}\right|_{rel} = \left(\sum_j^{TS} g_{iij}(0) Q_i(p)\right) \tag{12.17}$$

where $g_{iij}(0)$ are the vibrational cubic force constants of the isolate molecule. The corresponding *relaxation* effect on the vibrational frequencies is denoted by $\left(\frac{\partial \nu(p)}{\partial p}\right)_{rel}$.

Hence, the total effect of the pressure on the vibrational frequencies is partitioned as

$$\left(\frac{\partial \nu_i(p)}{\partial p}\right)_{\mathbf{Q}(p)} = \left(\frac{\partial \nu_i(p)}{\partial p}\right)_{cur} + \left(\frac{\partial \nu_i(p)}{\partial p}\right)_{rel} \tag{12.18}$$

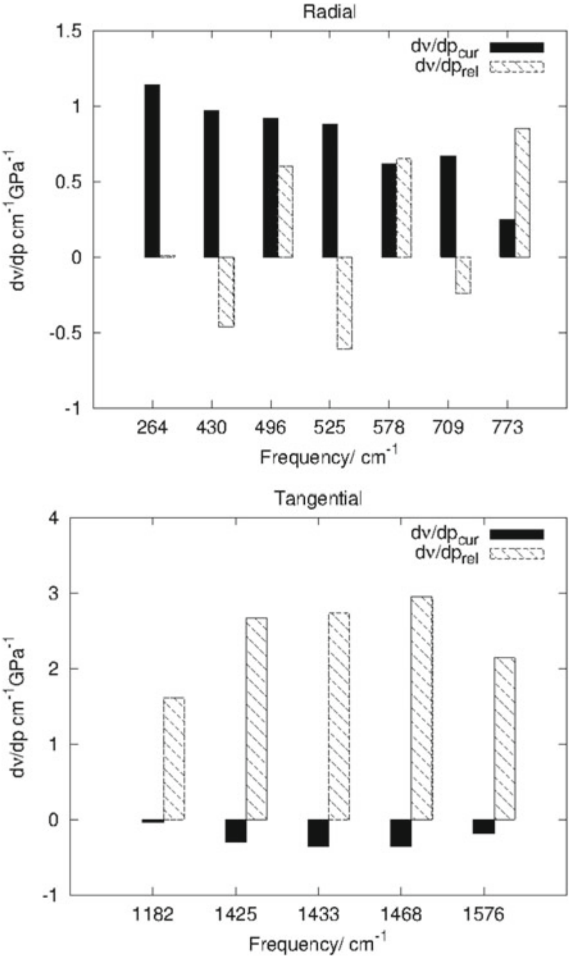

Fig. 12.6 XP-PCM analysis of the effect of the pressure on the vibrational pressure coefficients $(d\nu/dp)_{XP-PCM}$ (harmonic approximation) of Buckminsterfullerene. *Blue bars* correspond to the direct effect $(d\nu/dp)_{cur}$ (Eq. 12.15) and the *green bars* to the indirect contribution $(d\nu/dp)_{rel}$ (Eq. 12.16). The *upper panel* is pertinent to the normal modes with displacements of the nuclei along direction normal to the molecular surface of Buckminsterfullerene. The *lower panel* is pertinent to the normal modes with displacements of the nuclei along directions tangential to the molecular surface of Buckminsterfullerene. See Ref. [6] for computational details

The results of this partition into *curvature* and *relaxation* contributions are shown in Fig. 12.6 for the vibrational normal modes of fullerene $C60$. The different nature of the effect of the pressure on the radial and tangential vibrational normal modes of $C60$ is evident. The effect of the pressure on the frequencies of the radial normal modes is dominated by the *curvature* mechanism, due to the effect of the pressure on the electron density, while the effect of the pressure on the frequencies of the tangential normal modes is dominated by the *relaxation* mechanism, due to the shift of the equilibrium geometry induced by the pressure.

12.6 Conclusions

In this chapter, we have reviewed some recent developments in our XP-PCM method to introduce the effect of high pressure ($p > 1$ GPa) in the quantum chemistry study of molecular properties and processes.

Since a long time, theoretical chemists [25] have been aware that chemistry under extreme condition of pressure is a field where quantum chemistry should potentially exploit its predictive power to help predicting and understanding molecular processes. In spite of this awareness, the chemistry under extreme condition of pressure has been so far a territory distant from the frontiers of modern quantum chemistry. We hope that the XP-PCM model could help extending these borders, so to include even this territory within the domain of quantum chemistry.

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14. The energy eigenvalue E is not the basic energy quantity of the PCM-XP model. E refers to the total energy of the solute-solvent system with respect to a fictitious reference state, which depends on the wave-function $|\Psi>$. For more details on the status of the energy eigenvalue E see, for example, Ref. [2]
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