

Potential energy surface for the Pd–H₂ system: Comparison with matrix isolation experiments

Octavio Novaro^{1,*} and Cristina Jarque²

¹ Instituto Mexicano del Petróleo, Subdirección General de Investigación Aplicada, A.P. 14-805, 07730 México, D.F.

² Theoretical Chemistry Department, University of Cambridge, Cambridge CB3 9ET, UK

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Summary. We present here those aspects of the Pd–H₂ potential energy surface that are most directly related to the questions raised by matrix isolation experiments for the formation of Pd(η^1 -H₂) and Pd(η^2 -H₂) complexes. 125 points of this potential energy surface were obtained at a CI level using the CIPSI Scheme and including the order of 10⁵ configurations. Relativistic effects are included and shown not to be crucial in understanding the main features of the surfaces. The theoretical results serve to explain many features of the low-temperature experiments on the Pd–H₂ reaction, especially those concerning the spectroscopic changes observed when different noble gas supports, Kr or Xe, are utilized.

Key words: Potential energy surface – Pd–H₂ complex – *Ab-initio* CI calculations – Comparison with matrix isolation

1. Introduction

The theoretical predictions of our group [1] that H₂ was captured in end-on and side-on configurations by isolated Pd atoms were immediately confirmed experimentally by Ozin and Garcia-Prieto [2]. They found that the formation of the PdH₂ complex was spontaneous when Pd atoms are deposited on H₂-doped noble gas matrices at 12 K. This was perhaps the first instance concerning transition metal atoms in which a ligand-free molecular dihydrogen complex was observed [2]. Our own calculations [1] had shown that both the end-on and the side-on approaches of H₂ towards Pd had attractive curves so that these structures should form spontaneously and, in principle, both could be stable since their stabilization energies were of the order of 10 kcal/mol (they differed among themselves by only a few kcal/mol). We also found that the relaxation of the H–H distance was minimal (i.e. no scission of the H₂ bond exists); this last result is quite at variance with experiments on H₂ capture and activation by other metal atom [3] and with our theoretical calculations on Cu + H₂ [4] and

* On Sabbatical leave from Instituto de Física, UNAM

Pt + H₂ [5] reactions. This, notwithstanding the experiments on PdH₂, showed [2] that the H–H stretching mode was at such a high frequency and has such a low intensity that our prediction of small H–H bond relaxation was justified. This is also supported by calculations on the Pd–H₂ side-on structure [6–9].

Our prediction that both the side-on and end-on structures are stable was confirmed by matrix isolation studies using a Kr matrix: H₂, HD and D₂ isotopic substitution experiments [2] revealed two coexistent products Pd(η^2 -H₂) and Pd(η^1 -H₂). However, only the Pd(η^2 -H₂) product was observed when the noble gas matrix was changed to Xe [2]. This led to the conclusion that energy differences between Pd(η^1 + H₂) and Pd(η^2 + H₂) had to be small, of the order of magnitude of the ‘innert’ matrix interactions in fact, so that a small change of matrix (Kr to Xe) may induce such modifications in the coordination modes of the PdH₂ complex. We will show here that even if energy differences are not small, the particular form of the energy curve connecting the products may still explain these matrix effects. This in turn implies the necessity of obtaining more precise and wider-ranging studies on the Pd + H₂ potential energy surface in order to understand all these data. Consequently, we have calculated over ten times as many configurations of Pd–H₂ as those in [1] including several new geometries, thus obtaining a substantial part of its potential surface.

2. Method

We present here a series of studies on the Pd–H₂ potential surface which were carried out with the same methods of [1], namely the PSHONDO-CIPSI sequence of programs [10, 11], and the same basis sets and pseudo-potential [1, 12, 13]. A substantial part (125 points) of the Pd + H₂ potential energy surface was studied by varying the structural parameters of this three-center complex. For each point we carried out a SCF calculation of the closed shell Pd($d^{10}s^0$)¹S + H₂(¹ Σ_g^+) system followed by a variational-perturbational CI scheme including several hundreds of thousands of configurations and using the Møller–Plesset procedure of the CIPSI scheme [11].

Two important effects had to be tested in the present calculations: relativistic effects and superposition errors. Previous studies [12, 13] on Pd interactions with ethylene and other hydrocarbons, as well as in palladium clusters, have shown that superposition errors are important, and the use of the counterpoise correction following Kołos [14] is necessary to correct such errors.

Results on the side-on structure of Pd–H₂ using relativistic pseudo-potentials do exist [6–7]. Our previous calculations [1] did not include relativistic effects, so we must assess their importance before building the complete Pd–H₂ potential energy surface. For this the relativistic pseudopotential of La John et al. [15] (the same used in [7]) was utilized to test some of the curves already studied in [1]. The comparison of our new relativistic results with the non-relativistic calculations of [1] are given in Figs. 1–3. Both the relativistic and non-relativistic curves were corrected using the method of Kołos [14] to eliminate their respective superposition errors (which amount to an average of 4 kcal/mol for the non-relativistic calculations and about 2 kcal/mol for the relativistic). We show in Fig. 1 the spontaneous capture of an unrelaxed H₂ molecule by Pd in a side-on approach, while Fig. 2 shows the similar capture for an end-on approach of Pd to H–H. Finally Fig. 3 shows the opening of the bending angle in the side-on Pd–H₂ system (cf. [7]). In other words Figs. 1–3 correspond to the Figures of [1]

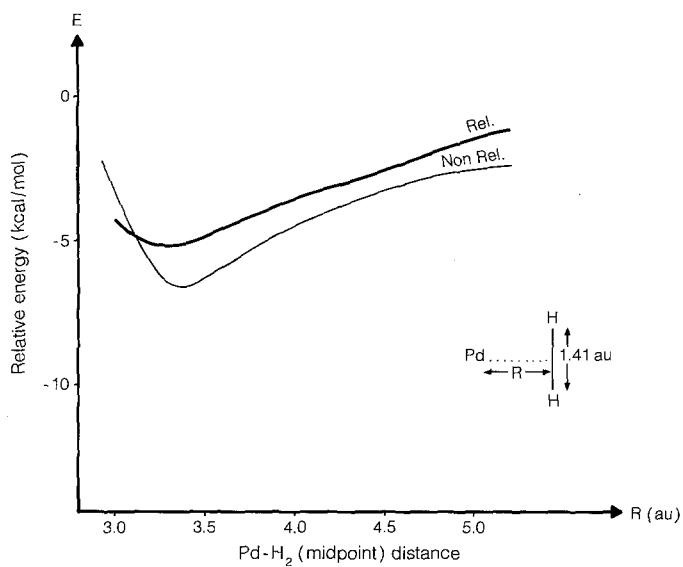


Fig. 1. Potential energy curve for the perfect C_{2v} symmetry (side-on) capture of an unrelaxed H₂ molecule by a palladium atom. The thin line gives the non-relativistic results, the thick line the relativistic ones. Both curves have been corrected for superposition errors using the counterpoise approximation

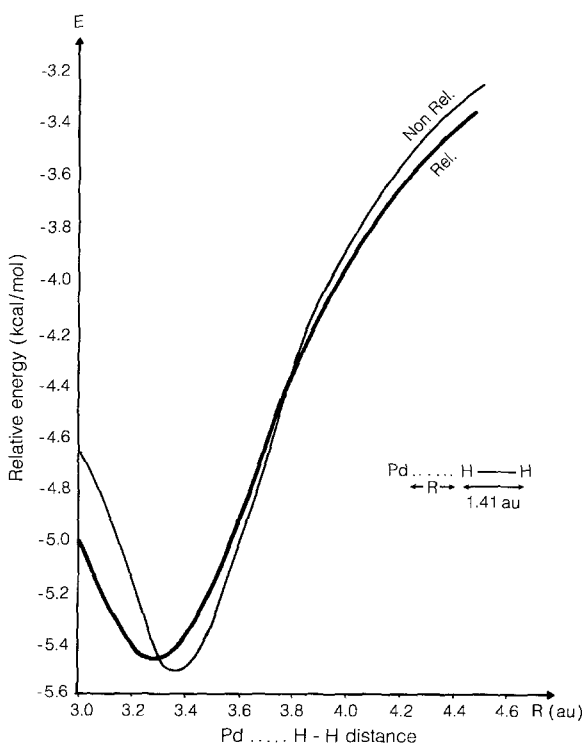


Fig. 2. Potential energy surface for the linear (end-on) capture of an unrelaxed H₂ molecule by a Pd atom. The thin line gives the non-relativistic results, the thick line the relativistic one. Both curves have been corrected for superposition errors using the counterpoise approximation

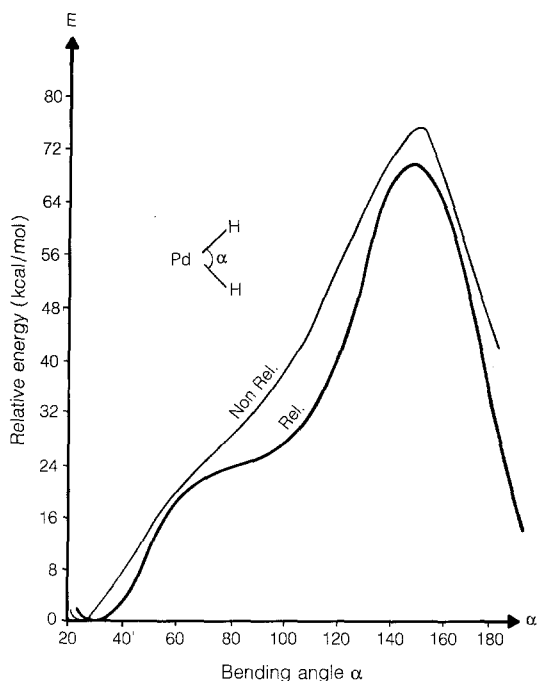


Fig. 3. Bending potential energy curve for the ground state (C_{2v} symmetry) of the PdH_2 system. The thin line gives the non-relativistic results, the thick line the relativistic ones. Both curves have been corrected for superposition errors using the counterpoise approximation

but including the counterpoise corrections and contrasting the non-relativistic results of [1] with those using the relativistic La John [15] potential. The general behaviour of the relativistic and non-relativistic curves is evidently very similar and apparently the relativistic effects are not too crucial for the description of the PdH_2 potential energy surface; in fact relativistic corrections are systematically smaller than superposition error corrections. Consequently, and in spite of the fact that all of the main features of the Pd-H_2 interactions were always tested both at a relativistic and non-relativistic level, the potential energy surface reported in the following section is a non-relativistic approximation. This will suffice to answer all the questions raised by matrix isolation experiments [2].

To plot the potential energy surface of PdH_2 we utilized an analytical fit following the theory of Murrell and co-workers [6]. The resulting potential function for the 1A_1 representation of the PdH_2 complex is of the form:

$$\begin{aligned}
 V_{\text{PdH}_2}(R_1, R_2, R_3) = & V_{\text{Pd}}^{(1)} + V_{\text{H}}^{(1)} + V_{\text{H}}^{(2)} + V_{\text{PdH}}^{(2)}(R_1) \\
 & + V_{\text{PdH}}^{(2)}(R_2) + V_{\text{H}_2}^{(2)} + V_{\text{H}_2}^{(3)} + V_{\text{PdH}}^{(3)}(R_1 R_2 R_3)
 \end{aligned}
 \tag{1}$$

where $V^{(3)}(R_1 R_2 R_3)$ is the purely non-additive three-body potential energy surface (see for instance [17] and the references therein). Equation (1) involves only ground states of the complex and its included diatoms and molecules making the function single valued and continuous. The functional forms of the different terms of Eq. (1) as well as the transformation matrix that guarantees its permutational symmetry are given in detail in [16]. Finally, the analytical form of these results was plotted as a three-dimensional surface using the Pot 3 program [16].

3. Results

We now present some parts of the PdH₂ potential energy surface which were obtained using the methods described in the previous section. We shall only report here those aspects of the surface that are related to the questions raised in Sect. 1, mainly the regions around the end-on and side-on structures that were predicted theoretically in our previous studies [1] and observed experimentally by Ozin and García-Prieto [2]. Among the spectroscopic results of [2] which merit a theoretical justification, several findings stand out. The low intensity band in the high frequency region for the IR spectra suggests the stretching of a slightly relaxed H-H bond but not a bond scission. In addition, the splitting of the IR bands found when the matrix was doped with HD implies the existence of two inequivalent hydrogen atoms, i.e. an end-on Pd··H-H complex. Also, and perhaps most importantly, there is the question of whether the coexistence of the two structures Pd(η^1 -H₂) and Pd(η^2 -H₂) is observed in matrix isolation experiments; this is reinforced by the fact that the additional band splitting of the IR bands when HD is used is never observed in Xe supports. Finally, they find that very high resolution IR scans show a double splitting for Pd(η^2 -H₂) sites in Xe but not in Kr while the Pd(η^1 -H₂) site in Xe shows a rotational progression of about 12 cm⁻¹ superimposed on the ν (Pd-H₂) IR band around 771 cm⁻¹. The latter dynamical effect implies an end-on structure that cannot be linear, but rather is bent.

All these questions can be understood from the form of the potential energy surface for the isolated PdH₂ complex. In Fig. 4 we present the region of the potential energy surface around an equilibrium H₂ molecule showing that the side-on approach of Pd to it is the most stable, yet a displacement of the metal atom to either of the equivalent linear Pd-H-H sites implies rather small energy changes. In fact the mobility of Pd around the H-H moiety is quite remarkable so that small temperature effects allow the free movement of Pd or equivalently, for a fixed Pd atom position the H₂ molecule is relatively free to move around without lessening its attachment to this Pd site. A similar situation has been found for the movements of the H₂ molecule around a palladium dimer [8]. In a future publication we will discuss this particular property of Pd_xH₂ complexes as contrasted with, for instance, Pt_xH₂ complexes which exhibit strongly fixed

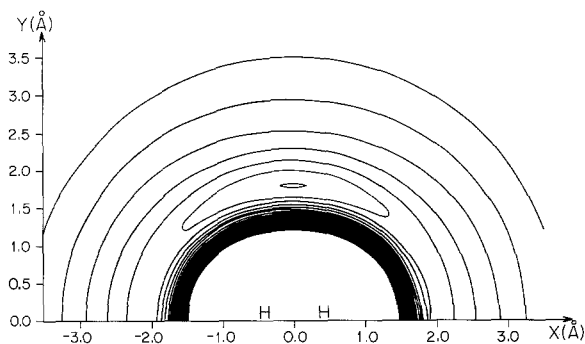


Fig. 4. Section of PdH₂ potential surface which shows the potential energy contours (each interval equals 0.25 eV) around the unrelaxed H₂ molecule. We see that the Pd atom is preferentially situated at or near a C_{2v} symmetry configuration, with Pd-H separations of about 1.83 Å. This is a manifestation of the preference for a side-on capture of H₂ by the atom. Notice, however, that the displacement of the Pd moiety from a C_{2v} symmetry only causes small energy changes

orientations and significant relaxation of the H–H bond. The relation of these properties of small Pd– and Pt–H₂ complexes to the quite different behaviour [19] of bulk palladium and platinum with respect to bulk absorption, surface adsorption, chemisorption and catalysis activation of hydrogen seems rather intriguing; as mentioned above, this will be discussed elsewhere.

In Fig. 5 the movement of a H atom towards a fixed Pd–H moiety is depicted, showing uncontestably that the H atoms prefer to stay attached to each other, i.e. that Pd is not really effective in provoking H–H scission. As this has already been discussed by us [1] and others [2] we shall not dwell on it for too long.

Part of the PdH₂ potential surface is depicted in Fig. 6, and it shows the simultaneous movement of a H and a Pd atom. The region represented in Fig. 6 is limited in the sense that only perpendicular displacements of Pd and H are given. The decrease in energy as the Pd atom approaches from infinity allows for the stabilization of the Pd(η^2 -H₂) product observed in [2], but on the other hand, the actual insertion of Pd on the H–H bond is hindered by the steep barrier on the bottom left hand side of Fig. 6. We may remember the case of CuH₂ where the metal's insertion into the H–H bond led to deep energy minima (in fact there

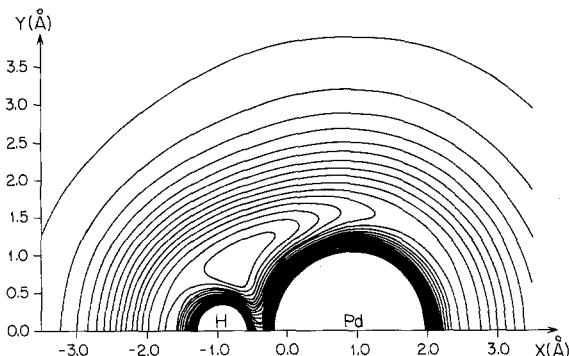


Fig. 5. Section of the PdH₂ potential surface around a fixed Pd–H atom separation of 1.83 Å. The other H atom is seen to be preferentially located at a rather mobile position, but that its optimal separation to the fixed H moiety does not differ by more than 10% from the H–H separation of an isolated hydrogen molecule

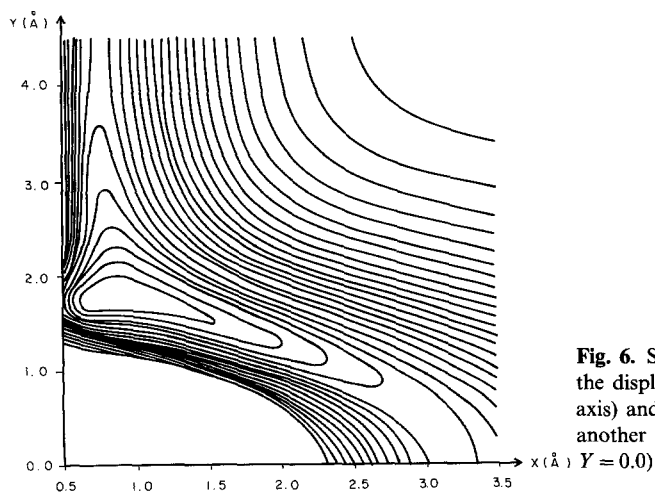


Fig. 6. Section of PdH₂ surface for the displacement of an H atom (*X* axis) and a Pd atom (*Y* axis) about another H atom (located at *X* = 0.0, *Y* = 0.0)

were two: a bent and a linear H-Cu-H structure) that in turn lead to the formation of the final CuH + H products [4]). This is in total contrast with the picture that the present PdH₂ energy surface gives, where the mobile H moiety must be dislodged rapidly from the other H atom and displaced far away (≥ 3 Å) to allow Pd to move any closer.

The most important issue raised by the matrix isolation experiments on the PdH₂ complex may be the coexistence of the two structures Pd(η^1 -H₂) and Pd(η^2 -H₂) in the Kr matrix but the absence of the first one in a Xe matrix. These structures correspond to the two minima already studied in [1]: the end-on and the side-on geometries.

We obtain here a more favorable energy for the side-on capture than for the end-on, as shall be discussed shortly. We are also interested in studying the torsional shift that would connect both of the structures which were reported as stable forms of PdH₂ in [1], in order to understand the low temperature experiments better [2]. As shown in Fig. 7 those two structures – the side-on and the end-on forms – are connected by a potential energy curve that does not present any activation barrier, thus making the former the only stable form for isolated PdH₂. The minimum in this curve corresponds to the following parameters: Pd-nearest – H distance = $3.266a_0$, Pd-farthest – H distance = $3.32a_0$ and H-H distance = $1.48a_0$.

The fact that the Kr matrix has far more constrained sites than Xe [2] indicates that the freedom of the H₂ moiety to reach the absolute minimum of the potential energy is hampered by the Kr matrix. The Kr matrix preserves the

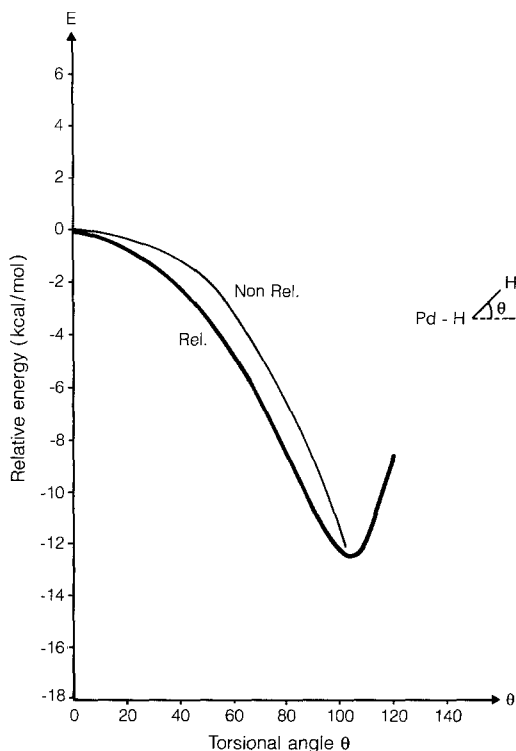


Fig. 7. Potential energy curve for the PdH₂ system as a function of the torsional angle which leads from the end-on to the side-on configurations ($\theta = 0^\circ$ represents the linear complex, $\theta = 102.55^\circ$ the perfect C_{2v} symmetry). The thin line gives the non-relativistic results, the thick one gives the relativistic results

linear end-on geometry or else of the intermediate bent structures of Figs. 5 and 7, while Xe is unable to do so. Further evidence of this capacity of Kr to hinder is the lack of the doublet splitting for a librational mode which is unique to Xe [2].

As reported in [2], a very high resolution IR scan shows a specific splitting for $\text{Pd}(\eta^1\text{-H}_2)$ sites in Kr showing a rotational progression of about 12 cm^{-1} superimposed on the $\nu(\text{Pd-H}_2)$ IR band around 771 cm^{-1} . This dynamical effect implies an end-on structure that cannot be linear, but rather is bent. Such structures had never been calculated before but correspond to the angles 0° and 60° in Fig. 7. The hindering effect of the Kr matrix (but not Xe) would allow their stabilization which in turn would lead to the observed rotational progression [1].

Therefore the presence of a linear $\text{Pd}(\eta^1\text{-H}_2)$ structure together with the energetically more stable bent $\text{Pd}(\eta^2\text{-H}_2)$ forms is a natural effect when a constraining rare gas matrix as Kr is used in the experiments.

4. Conclusions

The present results concerning the PdH_2 potential energy surface supplement our previous calculations [1] on the $\text{Pd}(\eta^1\text{-H}_2)$ and $\text{Pd}(\eta^2\text{-H}_2)$ complexes and allow us to understand fully all of the IR and Visible-UV observations [2] on these matrix isolated structures. In effect, the relatively mobile position of Pd around an H_2 molecule (Fig. 4), and the lack of capacity of the metal to activate the H-H bond (Fig. 5) or insert into it (Fig. 6) had been observed experimentally [2]. The energy pathway connecting the side-on and end-on geometries is barrierless and very flat for large angular deviations away from the linear end-on geometry (Fig. 7). Therefore the presence of the end-on structure together with the energetically more stable side-on form when a constraining rare-gas matrix such as Kr is used in the experiments [2] is to be expected. This end-on structure may be found in a perfectly linear form or bent at various angles of up to $\theta = 60^\circ$, as Figs. 5 and 7 show. This in turn explains the observation of rotational splittings of the $\nu(\text{Pd-H}_2)$ IR lines observed by Ozin and García-Prieto [2] on Kr matrices. All in all, we may conclude that our theoretical studies, including both the original prediction of spontaneous matrix isolation formation of $\text{Pd}(\eta^1\text{-H}_2)$ and $\text{Pd}(\eta^2\text{-H}_2)$ [1] and the present efforts to explain every spectroscopic finding of the experiments [2], yield satisfactory results.

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References

1. Jarque C, Novaro O, Ruiz ME, García-Prieto J (1986) *Am Chem Soc* 108:3507
2. Ozin GA, García-Prieto J (1986) *J Am Chem Soc* 108:3909
3. Ozin GA, McCaffrey JG, McIntosh DF (1984) *Pure Appl Chem* 56:11

4. García-Prieto J, Ruiz ME, Poulain E, Ozin GA, Novaro O (1984) *J Chem Phys* 81:5920; García-Prieto J, Ruiz ME, Novaro O (1985) *J Am Chem Soc* 107:5635
5. Poulain E, García-Prieto J, Ruiz ME, Novaro O (1986) *Int J Quantum Chem* 29:1181
6. Low J, Goddard WA (1984) *J Am Chem Soc* 106:8321
7. Balasubramanian K, Feng PY, Liao MZ (1988) *J Chem Phys* 88:6955
8. Brandemark UB, Blomberg MRA, Peterson LGM, Siegbahn PEM (1984) *J Phys Chem* 88:4617
9. Nakatsuji H, Hada M (1986) In: Smith VH (ed) *Applied Quantum Chemistry*. Reidel, Amsterdam, 1986, pp 93–109
10. Barthelat JC, Durand Ph, Serafini A (1977) *Mol Phys* 33:159
11. Huron B, Rancurel P, Malrieu JP (1975) *J Chem Phys* 58:5745
12. Jarque C, Novaro O, Ruiz ME (1987) *Mol Phys* 62:129; García-Prieto J, Novaro O (1980) *Mol Phys* 41:205
13. Daudey JP, Jeung G, Ruiz ME, Novaro O (1982) *Mol Phys* 46:67; Ruiz ME, Daudey JP, Novaro O (1982) *Mol Phys* 46:853
14. Kotos W (1979) *Theor Chim Acta* 51:219
15. La John LA, Christiansen PA, Ross RB, Atashroo T, Elmer WC (1987) *J Chem Phys* 87:2812
16. Murrell JN, Carter S, Farantos SC, Huxley P, Varandas AJC (1984) *Molecular Potential Energy Functions*. Wiley, Chichester
17. Ramírez-Solís A, Novaro O, Ruiz ME (1987) *Phys Rev B* 35:4082; Ramírez-Solís A, Daudey JP, Novaro O, Ruiz ME (1990) *Z Phys D* 15:71
18. Nakatsuji H, Hada M (1985) *J Am Chem Soc* 107:8264
19. Fast D (1976) *Gases in Metals*. McMillan, London