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Broken symmetry phase in solid *para*-hydrogen: Quantum mechanical calculation of the transition pressure at $T=0$

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Calculations of the broken symmetry phase-transition pressure at temperature (T) equal to 0 for *para*-hydrogen are presented. The calculations avoid simulation methods and determine the quantum mechanical states of a system of infinite rotors arranged in a regular lattice. In this way the quantum nature of the molecular rotational degrees of freedom is fully accounted for. In order to show the effect of correlations on a quantitative level, the calculations are performed both at the mean-field level and with correlations included. From the comparison with experimental results, information on the molecular length in the crystal at high pressure is obtained.

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I. INTRODUCTION

Solid *para*-hydrogen, when increasing pressure, undergoes a transition from an orientationally symmetric[1,2] to a broken symmetry phase (BSP).[2,3] The transition has been studied experimentally and has been found that, at low temperature (8 K), it takes place at a pressure of 110 GPa.[4]

In the following a simple interpretation of the transition is given. When the molecules are not too close (low pressure), so that they interact weakly and can thus be considered as almost free rotors, the fundamental state is the one in which all the molecules are in the isotropic, $J=0$, state (symmetric state). That is so because any rotational excitation would require kinetic energy that cannot be compensated by any other form of energy. However, when the molecules interact strongly (high pressure), the transition to excited rotational states can be compensated by the decrease in the potential energy. Actually, molecules in the excited rotational states, contrary to those in the spherically symmetric ground state, can orient and find the most favorable angular configuration. It is thus clear that the transition pressure gives information on both the rotational excitation energies and on the orientation-dependent intermolecular potential.

The problem of the BSP transition has been treated theoretically in many papers. At first the problem was faced in the mean-field approximation on a rigid-lattice model.[5,6] The molecules were treated as rigid rotors with their centers of mass sitting on the lattice sites. Moreover, it was assumed that the system orders in the fcc-$Pa3$ structure, and a gas phase intermolecular potential was used. The numerical results of these theories underestimate the transition pressure.

Correlation effects have been taken into account in various ways: by means of Jastrow-type variational wave function[7] and in a calculation based on the Green's function formalism.[8] The results of these works show that correlation effects tend to increase the transition pressure but are not sufficient to obtain the agreement with the experimental results.

A time-dependent Hartree formalism[9] has also been used to determine the transition pressure from the appearance of a roton soft mode. In this calculation it has been shown that translation-rotation coupling has a minute effect on the transition pressure.

The BSP has been studied also by means of methods involving simulation techniques. Quantum Monte Carlo calculations were performed to solve the quantum many-body problem both for the electrons and protons.[10] The calculation was performed for various structures, and a transition pressure of about 1 Mbar was found. Also path-integral Monte Carlo (PIMC) methods have been used together with an effective intermolecular potential derived from local-density approximation (LDA) calculations.[11,12] In Ref. 11 calculations of the transition pressures at low temperature are made for two different structures. The transition pressure depends on the lattice assumed (either fcc or hcp) and is even found to be too large if the hcp lattice is taken.

In this paper a method similar to the one described in Ref. 8 will be used. In such a method the lattice and orientational structures are assumed, and the (rotational) energies of the symmetric and BSP states are compared. In this calculation the interaction of translations and rotations is neglected, that is, the centers of mass of the molecules are assumed to be fixed at the lattice sites. Moreover, it is assumed that the anisotropic part of the intermolecular potential can be represented by a "reduced" form of the gas phase intermolecular potential, which is adapted to reproduce LDA results for the energy of the system.[11]

At first the mean-field method is used to calculate the molecular rotational energies that are later considered as zeroth-order energies. Then perturbation theory is applied to take account of the energy that is not included in the mean-field method. The energy of the symmetric orientationally disordered state is calculated up to third order and the one of the BSP state is up to second order.[8] The results of the present method are in close agreement with PIMC calculations.[11]

The present method, though limited to 0 K, is computationally much simpler than the PIMC method and allows many different computations, where some of the parameters characterizing either the intermolecular potential or the molecular properties can be varied. Moreover, the present method is not affected by the typical approximations contained in simulation techniques: limited systems and finite length of the Monte Carlo runs.[10] It actually treats an infinite system of rotors and the quanticity of the orientationally degrees of freedom if fully accounted for. It is affected by other approximations and limitations, mostly the perturbative method, but it is, however, useful because it can always be used also as a complementary method to test the results of more sophisticated techniques.

As already anticipated, the method needs a particular structure to be chosen. In the first studies of the BSP transition, it was suggested[5,6] that *para*-hydrogen assumed the fcc-$Pa3$ structure, which is the same as that of *ortho*-hydrogen at low pressure.[2] Later it has been proven that the centers of mass of the molecules form a hcp structure also in the broken symmetry phase.[13] There is no uniformity of views with regard to the orientations though. Among the most recent proposed orientational structures there are the $Pca2_1$,[14–16] the $P2_1/c$,[17,18] the $Cmc2_1$ (Ref. 19), and the incommensurate structures with $Pa3$ local order[12] demonstrated for the BSP in deuterium.[20]

In this paper the hexagonal compact structure for the centers of mass of the molecules is assumed with molecules oriented according to $Pca2_1$. Indeed, calculations performed with the present method (not reported here) show that the $Pca2_1$ orientational energy is lower than the energy of both the $Cmc2_1$ and $P2_1/c$ structures at the transition pressure. Other structures could have a lower energy, though, particularly the above-mentioned incommensurate one. From this point of view the present choice is only partly justified.

Moreover, the chosen structure is not an ideal one. For instance, the c/a ratio is smaller than the ideal value of $\sqrt{8/3}$ (Ref. 21), and the b/a ratio is estimated less than the ideal value $\sqrt{3}$ by *ab initio* molecular-dynamics simulation.[15] In principle crystal-field effects could affect the estimate of the transition pressure.[22,23] Such an effect depends on the deviations of c/a and b/a from their ideal values. However, the deviations estimated in Refs. 15 and 21 are not significant for hydrogen at low temperatures and will thus be neglected here.

The strict dependence of the transition pressure on both intermolecular potential and rotational energies makes it possible to obtain information on those quantities. In this paper an intermolecular potential is assumed, and consequently information on the rotational energies that allows a rough estimate of the molecular length will be obtained. The chosen potential[11] is built in such a way as to be compatible with the potential energy derived by LDA calculations. It is a pairwise potential containing the same spherical components as the one derived in Ref. 24 but with a reduction factor that depends on density.[11]

It is maybe worth pointing out the fact that also the problem of the triplet structure for the $S_0(0)$ transition is sensitive to the intermolecular potential and to the rotational excitation energy.[25–28] In that case it was found that the width of the triplet calculated by a gas phase potential was too large if compared with the experimental width at high pressures and that the rotational constant has to be considered as pressure dependent in order to have agreement with the measured triplet center. Particularly, at large pressures, it is found that the molecular length is to be increased with respect to the length of the molecule in the gas phase. Such a result has also brought speculations about a possible appearance of electron exchange between different molecules.[25]

The method outlined before will be applied in Secs. II and III to calculate the transition pressure as a function of the molecular rotational constant (B). The comparison of the calculations with the measured transition pressure is then used to estimate B and consequently the molecular length.

In Sec. II, results of the mean-field theory will be presented. It will be shown that the "mean-field" transition pressure is always lower than the experimental one. In Sec. III the method that takes into account the correlation effects will be presented. Finally, Sec. IV contains the numerical results for the transition pressure as a function of the rotational constant.

II. MEAN-FIELD CALCULATIONS

In the mean-field approximation the ground state of a system of rotors is a product of single rotor states, and the state of each rotor results from the averaged interaction with the other rotors.[2,5] As already stated in Sec. I, it is assumed here that the state resulting from symmetry breaking is the one in which the molecules are oriented in a particular structure ($Pca2_1$). Accordingly, for each lattice site i a preferred orientation $\hat{\Omega}_i$ is taken. The orientation of the molecule sitting in the site i will be denoted by $\hat{\omega}_i$. Moreover, $Y_{Jm}(\hat{\omega})$ indicates spherical harmonics with quantization axis along the lattice c axis. $Y_{Jm}^{\hat{\Omega}}(\omega)$ indicates spherical harmonics with quantization axis along the molecular symmetry axis $\hat{\Omega}$. The following relation holds:

$$Y_{J0}^{\hat{\Omega}_i}(\hat{\omega}_i) = \sqrt{\frac{4\pi}{2l+1}}\sum_m Y^*_{Jm}(\hat{\Omega}_i)Y_{Jm}(\hat{\omega}_i). \tag{1}$$

I indicate by $\phi(\hat{\omega}_i)$ the mean-field state for the single rotor i and assume that it can be expanded as a sum of spherical harmonics of order 0 with respect to the molecular symmetry axis,

$$\phi(\hat{\omega}_i) = \frac{1}{\sqrt{1+\sum_J |\lambda_J|^2}}\left[Y_{00} + \sum_J \lambda_J Y_{J0}^{\hat{\Omega}_i}(\hat{\omega}_i)\right] \tag{2}$$

with J as even integers starting from 2.

The λ_J coefficients can be obtained by minimizing with respect to them the total Hamiltonian of rotors averaged over the ϕ orbitals

$$\langle \phi(\hat{\omega}_1)\dots\phi(\hat{\omega}_N)|\left[\sum_i T_i + V(\omega^N)\right]|\phi(\hat{\omega})\dots\phi(\hat{\omega})\rangle, \tag{3}$$

where T_i is the rotational kinetic energy of molecule i, V is the orientation-dependent potential energy, and ω^N indicates a configuration of the collection of N rotors. In this calculation the potential energy is assumed to have the form of a sum of pairwise contributions[11,24]

$$V = \frac{1}{2}\sum_{i\neq j} V^{(2)}(\hat{\omega}_i\hat{\omega}_j). \tag{4}$$

Alternatively, the mean-field ground state can be obtained by solving the self-consistent differential equation

$$\left[T_i + \sum_{j(\neq i)} \langle V^{(2)}(\hat{\omega}_i \hat{\omega}_j)\rangle_j - \epsilon'\right]\phi(\hat{\omega}_i) = 0, \tag{5}$$

where $\langle V^{(2)}\rangle_j$ means averaging over orientations of molecule j.

$V^{(2)}$ contains both crystal-field and rotonic components. Because crystal-field effects can be safely neglected, only rotonic components are retained,

$$V^{(2)} = (4\pi)^{3/2}\sum_L v_{22L}(R_{ij})\sum_{m,n} C(22L;m,n,m+n)$$

$$Y_{2m}(\hat{\omega}_i)Y_{2n}(\hat{\omega}_j)Y^*_{Lm+n}(\hat{R}_{ij}), \tag{6}$$

where C are Clebsch-Gordan coefficients and $\vec{R}_{ij}$ is the vector joining site i with site j. The function $v_{22L}(R_{ij})$ depends on R_{ij}, which is the distance between i and j. In the case of a simple quadrupole-quadrupole interaction, $L=4$ and the function $v^{(2)}$ reads

$$v^{(2)}_{224}(R) = \frac{\sqrt{70}}{60}\frac{Q^2}{R^5} \tag{7}$$

with Q as the molecular quadrupole moment.[29]

In order to use either Eq. (5) or Eq. (3) it is useful to express the average energy per molecule as a function of the variational parameters λ_J. It is useful to know the following equations:

$$\langle\phi(\hat{\omega}_i)|T_i|\phi(\hat{\omega}_i)\rangle = BF(\lambda_J),$$

$$\langle\phi(\hat{\omega}_i)|Y_{lm}(\hat{\omega}_i)|\phi(\hat{\omega}_i)\rangle = G(\lambda_J)Y_{lm}(\hat{\Omega}_i), \tag{8}$$

with

$$F = \frac{\sum_J |\lambda_J|^2 J(J+1)}{\sum_J |\lambda_J|^2},$$

$$G = \frac{\sum_{JJ'} \lambda^*_J \lambda_{J'}\sqrt{(2J+1)}C(J2J':0,0,0)^2}{\sum_J |\lambda_J|^2}, \tag{9}$$

where the sums are extended to all even J and $\lambda_0=1$. Moreover, B is the rotational constant of the molecule, $B=\hbar^2/(2I)$, and I is the molecular moment of inertia. The function G is the reduction factor due to zero-point motion for the orientation of the molecule.[2]

It is now easy to show that

$$\langle\phi(\hat{\omega}_1)\ldots\phi(\hat{\omega}_N)|\left(\sum_i T_i + V\right)|\phi(\hat{\omega}_1)\ldots\phi(\hat{\omega}_N)\rangle/N$$

$$= BF(\lambda_J) + G(\lambda_J)^2 V_{\rm cl}, \tag{10}$$

where

$$V_{\rm cl} = V(\hat{\Omega}_1 \ldots \hat{\Omega}_N)/N \tag{11}$$

is defined as the potential energy per molecule with the molecules perfectly oriented along the axes $\hat{\Omega}_i$. In the following such an energy will be named *classical* potential energy because it does not contain the zero-point orientational motion.

TABLE I. Classical potential energy at the BSP transition in B units and λ_J coefficients.

$v_{\rm cl}$	λ_2	λ_4	λ_6
−6.806	0.320		
−6.652	0.398	0.037	
−6.651	0.398	0.037	0.002

Equation (10) shows the separation of kinetic (BF) and potential energy ($G^2V_{\rm cl}$) of the system of rotors. They both depend on the parameters λ_J. The kinetic energy has a minimum for $\lambda_0=1$ and $\lambda_J=0$ for all J's larger or equal to 2. The potential-energy contribution, on the other hand, diminishes when increasing λ_J's (if $V_{\rm cl}$ is negative, as is the case here).

Equation (10) can be rewritten by defining ϵ as the total energy and $v_{\rm cl}$ as the classical potential energy $V_{\rm cl}$ in B units,

$$\frac{\epsilon}{B} = F + G^2 v_{\rm cl}. \tag{12}$$

ϵ is to be minimized with respect to λ_J's. A minimum (eventually local) is obtained with all λ_J's equal to 0 for all J's different from 0 that corresponds to the orientationally disordered state. It will be named as the *symmetric* state in the following. When increasing the density, an energetically lower minimum with λ_J different from 0 starts to appear (BSP state). That happens when $v_{\rm cl}$ assumes a particular value. $v_{\rm cl}$ at the transition is derived by using an increasing number of λ_J's. In the table, $v_{\rm cl}$ at the transition is reported together with the λ_J values used in the derivation.

Table I shows that the transition takes place when the classical potential energy per molecule is, in absolute value, larger than the first-excited rotational state (six in B units). Table I shows also that there is an almost complete convergence of the transition value of $v_{\rm cl}$ with the maximum value of $J=6$.

In order to go from $v_{\rm cl}$ to density, hypotheses are to be done both for the intermolecular potential and for the rotational constant B. Here two cases will be considered: first the rotonic part of the gas phase potential ($V_{\rm gas}$) of Ref. 24 will be considered. It contains the three components with $L=0,2,4$. It is however interesting to notice that using a simple quadrupole-quadrupole interaction as in Eq. (7) with $Q=0.967$ a.u.,[29] the previous results for the transition pressure change by at most 1.5% at the largest B value.

In the second case the pairwise potential ($V_{\rm LDA}$) derived from LDA results[11] is considered, which is related to the gas phase potential $V_{\rm gas}$ by the density-dependent factor α,[11,12]

$$V_{\rm LDA} = \alpha V_{\rm gas},$$

$$\alpha = 0.61 + 0.31(R_{nn}/R^0_{nn} - 0.5), \tag{13}$$

with $R^0_{nn}=3.789$ Å.

In Fig. 1 the transition pressures are reported as a function of the rotational constant B. Mean-field pressures are reported with full and dashed lines: the former for the gas

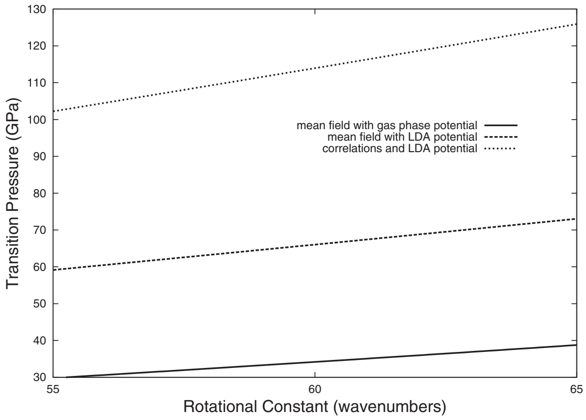

FIG. 1. Transition pressure as a function of the rotational constant B. Mean field with gas phase potential (full line), mean field with LDA potential (dashes), and mean field with correlations included and LDA potential (small dashes).

phase potential and the latter for the LDA potential. The comparison of the two curves shows the effect of the reduction in the intermolecular potential on the mean-field transition pressure. It is probably worth pointing out that the present calculations estimate the density rather than the pressure. In order to go from density to pressure, the equation of state of Ref. 21 is used here after a subtraction of thermal pressure is performed.[30] From the measured transition pressure of 110 GPa,[4] it is seen that it takes unreasonable values for the rotational constant to get agreement with the measured pressure.

In Sec. III correlation effects in the case of LDA potential will be taken into account: their importance will be stressed, and finally a value for the rotational constant will be estimated.

III. CORRELATION EFFECTS

By using Eq. (8), the self-consistent Eq. (5) can be written as

$$\left[T_i + G(\lambda_J)\sum_{j(\neq i)} V^{2)}(\vec{R}_{ij}\hat{\Omega}_j\hat{\omega}_i)\right]\phi(\hat{\omega}_i;\lambda_J) = \epsilon'\,\phi(\hat{\omega}_i;\lambda_J). \tag{14}$$

Due to the symmetry of the $Pca2_1$ structure, the effective potential felt by molecule i contains only spherical harmonics of zero order with respect to the $\hat{\Omega}_i$ direction. Keeping in mind the result and the definition of V_{cl}, the previous equation can be written as

$$\left[T_i + 2G(\lambda_J)V_{\mathrm{cl}}\sqrt{\frac{4\pi}{5}}Y_{20}^{\Omega_i}(\hat{\omega}_i)\right]\phi(\hat{\omega}_i;\lambda_J) = \epsilon'\,\phi(\hat{\omega}_i;\lambda_J). \tag{15}$$

The mean-field ground-state eigenfunction $\Psi_0(\omega^N)$ of the system of N rotors is given by the product of the single-molecule orbitals

$$\Psi_0(\omega^N) = \Pi_i \phi(\hat{\omega}_i) \tag{16}$$

and the mean-field total energy (E_0) reads

$$E_0 = N\epsilon, \tag{17}$$

where the energy per molecule ϵ is given by

$$\epsilon = \epsilon' - G(\lambda_J)^2 V_{\mathrm{cl}}. \tag{18}$$

The second term in the definition of ϵ avoids double counting of the pair interactions.

The same solution can be obtained as the eigenfunction of the ground state of the Hamiltonian H_0 is defined as

$$H_0 = \sum_i \left[T_i + G(\lambda_J)2V_{\mathrm{cl}}\sqrt{\frac{4\pi}{5}}Y_{20}^{\Omega_i}(\hat{\omega}_i) - G(\lambda_J)^2 V_{\mathrm{cl}}\right], \tag{19}$$

whereas the real Hamiltonian of the same system reads

$$H = \sum_i T_i + V(\omega^N). \tag{20}$$

Correlation effects will be estimated by treating perturbatively the difference between the real Hamiltonian H and the mean-field one, H_0,

$$H - H_0 = V(\omega^N) - G(\lambda_J)2V_{\mathrm{cl}}\sqrt{\frac{4\pi}{5}}\sum_i Y_{20}^{\Omega_i}(\hat{\omega}_i) + NG(\lambda_J)^2 V_{\mathrm{cl}}. \tag{21}$$

It is clear that, for the disordered state, $G(\lambda_J)=0$ and the perturbation is just the potential energy of the rotors.

At first order the correction E_1 to the energy is null

$$E_1 = \langle\Psi_0|(H - H_0)|\Psi_0\rangle = 0 \tag{22}$$

because Ψ_0 is a solution of the mean-field self-consistent equations.

In order to find the second (and higher)-order perturbative corrections, zeroth-order excited states of Eq. (15) are to be found. That will be done numerically by retaining only the rotational states up to $J=6$. The procedure is similar to that described in Ref. 5. The restriction to rotational quantum numbers that are lower or equal to six affects the excited rotational energy needed for the calculation for less than 1%. For the single-molecule orbitals, the projection of the angular momentum along the ordering axis $\hat{\Omega}_i$ is a constant of motion so that each orbital can be characterized by a quantum number μ. The other will be defined as k. Thus, an orbital can be expanded according to

$$\phi_{k\mu} = \sum_J^{6} \lambda_J^{k\mu} Y_{J\mu}, \tag{23}$$

where $\lambda_J^{k\mu}=0$ if $J<|\mu|$. k is chosen to be zero for the ground state. The relative energies will be denoted by $\epsilon_{k\mu}$.

Second (and higher)-order perturbative corrections can be derived by the application of standard formulas if zeroth-order eigenvalues and eigenfunctions are known, that is, when $\lambda_J^{k\mu}$ and $\epsilon_{k\mu}$ are known. In principle both single and double excitations are possible, that is, transitions from the state with all molecules in the $k=0$ to states with one or two molecules in states with $k\neq 0$. The contribution of the single excitation transitions is related to the crystal-field compo-

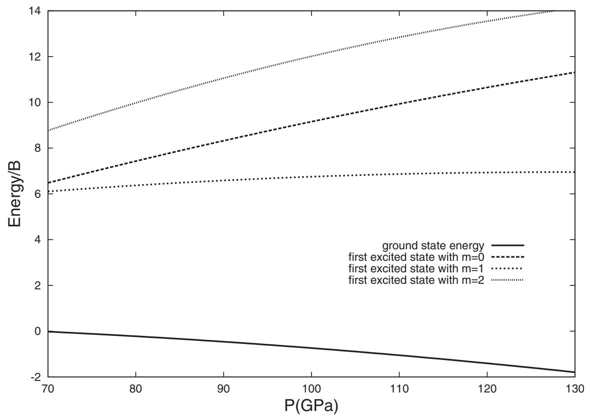

FIG. 2. Energies of the ground and first-excited rotational states in the mean-field approximation with $B=60\ \text{cm}^{-1}$. Ground state (line). Excited states: $m=0$ (long dashes), ±1 (short dashes), and ±2 (points).

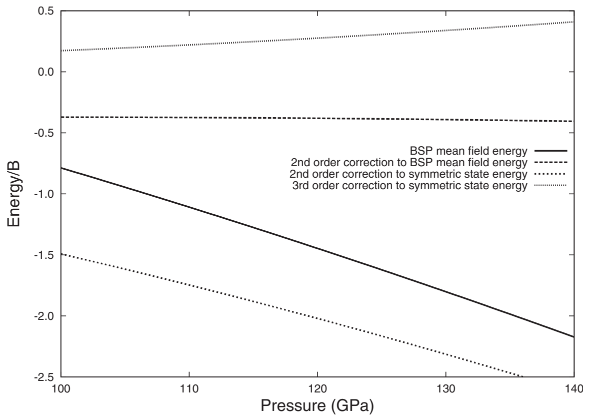

FIG. 3. Mean-field energy for the BSP state (full line), correlation effects at second order for the BSP state (long dashes), second-order correction for the symmetric state (short dashes), and third-order corrections to the symmetric state (points).

nents of the potential, and thus, it can be safely neglected[2] for the symmetry of the hcp structure. As already anticipated, the corrections are now calculated for the intermolecular potential determined from LDA results.[11]

In Fig. 2 the energies of the mean-field ground state and of the first-excited rotational states are reported, with $\mu=0,\pm1,\pm2$. The energies are reported as a function of pressure. It is seen that, in the range of pressures that is of interest here, the energy differences between the excited and the ground states increase with increasing pressure.

In the mean-field case, the symmetric state is described by orbitals independent of the molecular orientation ($\lambda_0=1$ and all other λ_J's equal to 0). Moreover, the energy is rigorously equal to zero. BSP states appear only after a critical density is reached, and it is only after the energy of the BSP state vanishes that we can speak of BSP transition in the mean-field approximation. One of the main effects of correlations is that the energy of the symmetric state decreases. Also the energy of the BSP state decreases but is less than the energy of the symmetric state. That is so because in the mean-field symmetric state only the kinetic rotational energy is taken care of, whereas in the mean-field BSP state some of the potential energy is also taken into account. For such a reason correlation effects increase the transition pressure, which is what is to be expected after comparing the measured transition pressure with that calculated in the mean-field approximation. One more consequence is the fact that second-order perturbative corrections to the energy of the symmetric state are usually larger than the analogous correction to the BSP state energy. For that reason, in the case of the symmetric state energy, also the third-order perturbative correction is calculated.

The energies for the symmetric and BSP states are reported in Figs. 3 and 4 for the particular case of $B=60\ \text{cm}^{-1}$. In Fig. 3 separate contributions are reported for different perturbative orders. From that figure information can be obtained on the uncertainty of the present calculations. The ratio of third- to second-order corrections to the symmetric state can be taken as the parameter measuring the rate of convergence of the perturbative expansion. At 110 GPa that quantity amounts to about 10%. Multiplying by 10% the highest perturbative orders for the two cases of symmetric and BSP states, it is found that the uncertainty on the total energies is about 1% for the symmetric state and 4% for the BSP state.

In Fig. 4 the total energies for the symmetric and BSP states are reported for a rotational constant of $B=60\ \text{cm}^{-1}$. It is seen that the two curves cross at a pressure of about 114 GPa. On the other hand, from the dependence of the energy on the pressure, it is easily found that a variation of 5% on the energy corresponds to a variation of about 2.5 GPa on the pressure. That is the uncertainty estimated here for the transition pressure calculated by means of the present method.

IV. RESULTS

The main result of this work is reported in Fig. 1. That figure shows both the effect of correlations and the dependence of the transition pressure on the rotational constant. Correlation effects are estimated by comparing curves with dashes and points. Dashes are reserved for the transition pressure derived by the mean-field method and points are for

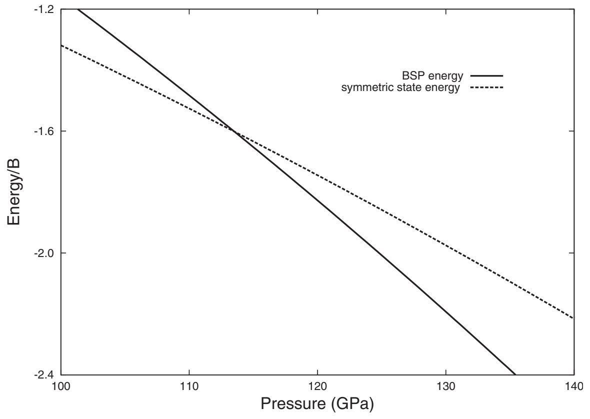

FIG. 4. Energy of the BSP state (full line) and of the symmetric state (dashes).

pressure estimated by also taking correlation effects into account. It is seen that correlation effects increase the transition pressure by almost a factor of 2 that is, thus, the order of magnitude of the effects due to correlations.

Next it is important to check the present method by comparing its results with those obtained in Ref. 11 with a quite different method. In that work PIMC calculations were performed both for deuterium and hydrogen at low temperature. Transition pressures of 49 and 120 GPa were determined for the hcp structure in the two cases. Those results have been obtained by assuming, for the rotational constants, the gas phase ones and using the equation of state reported in Ref. 30, particularly the one in the Vinet form. By performing the calculations for the transition pressures in the same conditions but with the present method, it is now found to be 47 and 125 GPa, which is in agreement with the previous calculations if the uncertainty estimated at the end of Sec. III is taken into account. This result is important because it demonstrates the consistency of two methods based on quite different approximations.

From Fig. 1 one can see the dependence of the transition pressure on the rotational constant. It is natural to use that dependence in order to determine the B value at the transition. As already mentioned, the measured transition pressure for hydrogen at low temperature is 110 GPa. A close inspection of Fig. 1 shows that the measured transition pressure is reproduced for a value of the rotational constant of 58.2 cm^{-1}. That value is affected by an uncertainty, as pointed out in Sec. III for the transition pressure, which for the rotational constant amounts to about 1 cm^{-1}. Consequently the rotational constant at the transition pressure is determined in a range varying from the gas phase value (59.3 cm^{-1}) (Ref. 31) down to about 57 cm^{-1}, that is, it can decrease by at most 4% with respect to the gas phase value. Such a decrease in the rotational constant means an increase in the intramolecular length by at most 2%.

Indeed, other works point out that when pressure is large enough, the intramolecular distance increases.[25–28] In those papers the decrease in B was determined by the analysis of the Raman $S_0(0)$ triplet, that is, at pressures smaller than the BSP transition pressure. Moreover, it was found that the decrease in B, and thus, the increase in the intramolecular length, was larger than the one found here (about 5% at 80 GPa).[28] That is not completely satisfactory, though, at least in view of the interpretation of the increase in the intramolecular length as an effect of transfer of electronic charge from the intramolecular to the intermolecular region.[25]

In the end, in this work, the BSP transition pressure of *para*-hydrogen at $T=0$ has been calculated as a function of the molecular rotational constant. From the comparison of calculated and measured transition pressures, it is found that the molecular rotational constant is smaller at the BSP transition pressure than in the gas phase, indicating an increase in the molecular length under pressure. This is in qualitative agreement with similar results obtained by the analysis of the rotational Raman spectrum.

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