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Calculation of MP_2 and Coupled-Cluster Molecular Properties Using the q-Integral Method[†]

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The main purpose of this paper is to report results of quantum mechanical calculation of the H_2 system using the q-Integral method with correlation corrections to the SCF (Self Consistent Field) wave functions included through the Møller−Plesset second-order perturbation (MP_2) and Coupled-Cluster (CC) theory. Using the q-Integral method, we evaluated potential energy curves, rovibrational spectroscopy constants, rovibrational spectra, interatomic equilibrium distance and longitudinal static hyper(polarizability). All calculations were carried out through the STO-3G, STO-6G, and *double*-ζ (DZV) atomic basis set. The q-Integral method was implemented in the source code of the general ab initio quantum chemistry package GAMESS.

1. Introduction

The challenge of modern ab initio methods of electronic structure is to perform highly accurate calculations at a lower computational cost. An alternative way to accomplish this goal is through the development of scaling algorithms of important quantities such as: one and two-electron integrals, Fock operator, molecular orbital, etc. An indicator of the cost size of a computational method is the behavior of its scaling. Scaling behavior is usually expressed as N^{α}, where N is the number of the base functions involved in the calculation and α refers to the scaling exponent, which indicates how the computational cost of the method increases with the number of base set function. For example, MP_2 electron correlation methods,[1] CCSD,[2] CCSD(T),[3] CCSDT,[4] and CCSDTQ[5] scale with N^5, N^6, N^7, N^8, and N^{10}, respectively. This means that doubling the number of base functions makes the computational cost of these methods increase by factors of 32, 64, 128, 256, and 1024, respectively.

One of the most traditional methods of electronic structure is the Hartree−Fock method (HF),[6−9] which is, formally, cited as a method that scales with N^4. This scaling of N^4 comes from the number of integrals of two-electron (N_{2e}) and four-centers, as follows

$$\langle\mu\nu|\lambda\sigma\rangle = \int\int \phi_{\mu}(1)\,\phi_{\nu}(1)\frac{1}{r_{12}}\phi_{\lambda}(2)\,\phi_{\sigma}(2)\,d\tau_1\,d\tau_2 \qquad (1)$$

where μ, ν, λ, and σ are the atomic orbitals. However, many two-electron integrals have a negligible value and can therefore be discarded a priori. However, the computational cost of the HF method in a large molecular system can be drastically reduced using the inequality of Schwarz,[10]

$$|\langle\mu\nu|\lambda\sigma\rangle| \leq \sqrt{\langle\mu\nu|\mu\nu\rangle\langle\lambda\sigma|\lambda\sigma\rangle} \qquad (2)$$

This relation allows a reduction in the calculation of integrals of two-electrons to $N^2 \log N$. In ref 11 it was shown analytically that (N_{2e}) scales as $N^2(\ln N)^2$. Subsequently, a methodology was proposed which found that N_{2e} scales as $N^2 \ln N$.[12] An estimate that N_{2e} scales as $N^{2.2-2.3}$ was reported in ref 13.

To minimize part of these computational problems, we proposed in ref 14 an alternative strategy to reduce the CPU time to calculate the two-electron integrals in ab initio molecular calculations. This was called the q-Integral method.[14,15] In the q-Integral method, the multicenter electronic integrals are described by analytic functions of the interatomic distances. This method reduces substantially the CPU time for calculation of bielectronic integrals used in calculations of ab initio molecular quantum mechanics. This approach makes it possible to write the bielectronic integrals as analytical functions of the internuclear distances, and consequently the electron energy is also a function of interatomic distances and LCAOs coefficients as $E = E[C_{\mu\nu\lambda\sigma}, q - I_{\mu\nu\lambda\sigma}(R)]$, where $q - I_{\mu\nu\lambda\sigma}(R)$ is called the q-Integral and R is the distance between nuclei A and B. More details about the q-Integral method are presented in the next section.

In this context and using contracted base functions ($\phi_{\mu}^{\mathrm{CGF}} = \sum_{p=1}^{L} d_p\phi_p^{\mathrm{GF}}$), we have

$$\begin{aligned}\langle\mu\nu|\lambda\sigma\rangle &= \int\int \phi_{\mu}^{\mathrm{CGF}}(1)\,\phi_{\nu}^{\mathrm{CGF}}(1)\frac{1}{r_{12}}\phi_{\lambda}^{\mathrm{CGF}}(2)\,\phi_{\sigma}^{\mathrm{CGF}}(2)\,d\tau_1\,d\tau_2\\ &= \sum_{p=1}^{L}\sum_{q=1}^{L}\sum_{s=1}^{L}\sum_{t=1}^{L} d_{p\mu}d_{q\nu}d_{s\lambda}d_{t\sigma}\int\int \phi_p^{\mathrm{GF}}(1)\,\phi_q^{\mathrm{GF}}(1)\times\\ &\qquad \frac{1}{r_{12}}\phi_s^{\mathrm{GF}}(2)\,\phi_t^{\mathrm{GF}}(2)\,d\tau_1\,d\tau_2\\ &= \sum_{p=1}^{L}\sum_{q=1}^{L}\sum_{s=1}^{L}\sum_{t=1}^{L} d_{p\mu}d_{q\nu}d_{s\lambda}d_{t\sigma}\langle pq|st\rangle\end{aligned} \qquad (3)$$

here

$$\langle pq|st\rangle = \int\int \phi_p^{\mathrm{GF}}(1)\,\phi_q^{\mathrm{GF}}(1)\frac{1}{r_{12}}\phi_s^{\mathrm{GF}}(2)\,\phi_t^{\mathrm{GF}}(2)\,d\tau_1\,d\tau_2 \qquad (4)$$

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where $r_{12} = |\vec{r}_2 - \vec{r}_1|$, $\vec{r}_i$ is the position vector of the electron i, the sets $\{d\}$ and $\{\alpha\}$ are the contraction coefficients and exponents, respectively, L is the number of contracted Gaussians functions used to expand the atomic orbital, and μ, ν, λ, and σ are the atomic orbitals.

Thus, we get a new scaling on the right side of eq 3 where for each integral of type $\langle\mu\nu|\lambda\sigma\rangle$ it is necessary to calculate L^4 integrals of the type $\langle pq|st\rangle$. So, formally, the total number of integrals of two-electron and four centers of type $\langle pq|st\rangle$ must be $N^4 \times L^4$. In the q-Integrals method, we see that each integral $\langle\mu\nu|\lambda\sigma\rangle$ must be represented by an analytical function of the interatomic distances (R), in other words,

$$\langle\mu\nu|\lambda\sigma\rangle = \text{analytical function}(R) \tag{5}$$

reducing the total number of two-electron integrals to N^4. It should be noted that the scaling methodologies, cited above, remain valid when added to the q-Integral method. The accuracy of these molecular properties can be obtained, in part, by including the electronic correlation (EC) effects.[16]

The main goal of this work is to examine the accuracy of the q-Integrals as a function of internuclear distance, through some levels of calculations, with inclusion of the correlation corrections to the SCF wave functions. However, instead of just comparing the values of the q-Integrals with the ones obtained by the traditional approach, we chose to compute properties which are very sensitive to the electronic integrals in function of the interatomic distance. To this end, we calculated the molecular properties of the H_2 system using the q-Integral method with EC effect included through the Møller–Plesset (MP_2) second-order perturbation[1] and Coupled-Cluster (CC)[2–5] theory. Today, CC theory has emerged as the most accurate, widely applicable approach for the correlation problem in molecules.

In this work, the q-Integral method was used in four cases using the MP_2 and CC (CCD and CCSD approach) theory: (i) to build up the potential energy curves (PEC) of the molecular system H_2 with the following atomic basis sets: STO-3G, STO-6G, and double-ζ (DZV), considering several interatomic distances varying between 0.5 and 5.0 bohr; (ii) to evaluate the spectroscopic constants and the rovibrational spectra for the related molecular system; (iii) to optimize the interatomic distance for the related molecular system; (iv) to calculate the static linear polarizability and second longitudinal static hyperpolarizability using two different approaches: the Coupled-Hartree–Fock (CPHF)[17] and Field Finite (FF)[18] methods.

This paper is organized as follows: In section 2 we present the computational details and the q-Integral method. Our results as well as the discussion are presented in section 3. In section 4, we display our conclusions.

2. Computational Details and q-Integral Method

The q-Integral method is based on the generalized exponential function.[19–21] The advantage of this procedure, when compared with the usual one, is that the CPU time for calculation of two-electron integrals is substantially reduced. The generalization of the exponential function was proposed by Borges[21] based on the Tsallis Statistics, in the following way:

$$\exp_q(r) \equiv [1 + (1 - q)r]^{1/(1-q)} \tag{6}$$

The parameter q comes from the Tsallis statistics[20] defined by a microcanonic ensemble, that is, $S_q = k(1 - \sum_i^W p_i^q)/(q - 1)$, where p_i are the probabilities associated with W microstates (configurations), k is a positive constant, and q is a real parameter that generalizes the usual statistics. In the limit $q \rightarrow 1$, the generalized q-Exponential function (eq 6) is equivalent to the usual exponential functional in the limit $q \rightarrow 1$ and the q-entropy goes to Boltzmann entropy as follows: $S_1 \equiv \lim_{q\rightarrow 1} S_q = -k\sum_i^W p_i \ln p_i$.

In a previous paper[15] we introduced the generalized Morse function (q-Morse) in the HF methodology,

$$\begin{aligned} M(r) \equiv\ & y_0 + \beta e_q^{-\alpha(R-R_0)^\gamma}(e_q^{-\alpha(R-R_0)^\gamma} - C) \\ \equiv\ & y_0 + \beta[1 - (1 - q)\alpha(R - R_0)^\gamma]^{1/(1-q)} \times \\ & ([1 - (1 - q)\alpha(R - R_0)^\gamma]^{1/(1-q)} - C) \end{aligned} \tag{7}$$

where y_0, α, β, q, R_0, γ, and C are adjustable parameters. To fit the two-electron integrals, using the q-Morse function, only these seven parameters are necessary. It is important to point out that the success of the fitting procedure is, in part, due to the q-Exponential function's flexibility.

In the eq 3, the number of the two-electron integrals $\langle pq|st\rangle$ scales with L^4. The sum of L^4 Gaussian integrals will be described by just one function, as follows,

$$\begin{aligned} q - I_{\mu\nu\lambda\sigma}(R) =\ & \langle\mu\nu|\lambda\sigma\rangle_q \\ \equiv\ & y_{0\mu\nu\lambda\sigma} + \beta_{\mu\nu\lambda\sigma} e_{q_{\mu\nu\lambda\sigma}}^{-\alpha_{\mu\nu\lambda\sigma}(R - R_{\mu\nu\lambda\sigma})^{\gamma_{\mu\nu\lambda\sigma}}} \times \\ & (e_{q_{\mu\nu\lambda\sigma}}^{-\alpha_{\mu\nu\lambda\sigma}(R - R_{\mu\nu\lambda\sigma})^{\gamma_{\mu\nu\lambda\sigma}}} - C_{\mu\nu\lambda\sigma}) \end{aligned} \tag{8}$$

where $y_{0_{\mu\nu\lambda\sigma}}$, $\alpha_{\mu\nu\lambda\sigma}$, $\beta_{\mu\nu\lambda\sigma}$, $q_{\mu\nu\lambda\sigma}$, $\gamma_{\mu\nu\lambda\sigma}$, $R_{0_{\mu\nu\lambda\sigma}}$, and $C_{\mu\nu\lambda\sigma}$ are parameters adjusted to fit the sum of all two-electron integrals in the contracted Gaussian form.

As eq 3 expresses the value of the two-electron integral as a function of the internuclear distance, the value of any integral $\langle\mu\nu|\lambda\sigma\rangle_q$ can be obtained, at any given interatomic distance R, just by inserting this value in eq 8.

In this methodology, the total electronic energy is given as a function of the interatomic distance through the two-electron integrals as follows:

$$E = E\{[C], q{-}I_{\mu\nu\lambda\sigma}(R)\} \tag{9}$$

more precisely,

$$E_{HF} = \sum_\mu \sum_\nu C_{\mu\nu}H_{\mu\nu} + \sum_\mu \sum_\nu C_{\mu\nu} \sum_\lambda \sum_\sigma C_{\lambda\sigma}\Big[\langle\mu\nu|\lambda\sigma\rangle_q - \frac{1}{2}\langle\mu\lambda|\nu\sigma\rangle_q\Big] \tag{10}$$

where $H_{\mu\nu}$ is one-electron part of the Hamiltonian and $q - I_{\mu\nu\lambda\sigma}(R) = \langle\mu\nu|\lambda\sigma\rangle_q$ is the q-Integral. The $C_{\mu\nu}$ are the coefficients of the molecular orbital expansion in terms of the atomic orbitals (LCAO). The indices μ, ν, λ, and σ, using the STO-LG basis set, can only assume two values (1 and 2) in case of the H_2 molecule. For a DZV basis set the indices μ,ν,$\lambda$and σ can assume values between 1 and 4, and the summation in eq 10 will involve a much larger number of terms.

In the q-Integral method, the electronic correlation energy in MP$_2$ (E_{MP2}) and CCD (E_{CCD}) methods can be written as

$$E_{\mathrm{MP}_2} = \sum_{\substack{i<j \\ a<b}} \frac{|\langle ij||ab\rangle_q|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \qquad (11)$$

and

$$E_{\mathrm{CCD}} = \sum_{i<j} \sum_{a<b} \langle ij||ab\rangle_q C_{ij}^{ab} \qquad (12)$$

where i, j stand for occupied and a, b for unoccupied orbitals. The quantities ε_i, ε_j, ε_a, and ε_b are the corresponding orbital energies and C_{ij}^{ab} is the cluster amplitude. In eqs 11 and 12 we introduce the notation: $\langle ij||ab\rangle_q = \langle ij|ab\rangle_q - {}^1/_2\langle ib|aj\rangle_q$.

The H$_2$ rovibrational spectroscopic constants were calculated using two different approaches: in the first one, the spectroscopic constants were obtained combining the rovibrational energies obtained through Schrödinger nuclear equation and the one below:[22]

$$E_{\nu J} = \omega_{\mathrm{e}}\left(\nu + \frac{1}{2}\right) - \omega_{\mathrm{e}}x_{\mathrm{e}}\left(\nu + \frac{1}{2}\right)^2 + \omega_{\mathrm{e}}y_{\mathrm{e}}\left(\nu + \frac{1}{2}\right)^3 + \ldots + \left[B_{\mathrm{e}} - \alpha_{\mathrm{e}}\left(\nu + \frac{1}{2}\right) + \ldots\right]J(J+1) \qquad (13)$$

where v and J are the vibrational and rotational levels, respectively. From this combination one can obtain the closed equations for rovibrational spectroscopic constants (see eq 13 in ref 15). To get the rovibrational energies, we solved Schrödinger nuclear equation using the Discrete Variable Representation method (DVR).[23] Another methodology used to evaluate the spectroscopic constants was that of Dunham,[24] which is obtained by comparing eq 13 and the potential energy curves (PEC) written with a Taylor expansion around the equilibrium distances. To use these approaches, it is necessary to know the analytical forms of the electronic energies for several nuclear configurations of the molecular system. The best fit was obtained using one analytical function based on a polynomial q-Bond Order (q-BO)[25] coordinates of the tenth degree.

In the presence of a static uniform electric field ($\vec{F}$) the perturbed energy (E) of a molecule can be written as

$$E(F) = E_0 - \sum_i \mu_i F_i - \frac{1}{2!}\sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{3!}\sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{4!}\sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l - \cdots \qquad (14)$$

where summations over the repeated indices are assumed. Here, E_0 is the energy of the molecule in the absence of an external electric field and μ_i are the components of the permanent dipole moment, α_{ij} are the components of the dipole polarizability, β_{ijk} are the components of the first dipole hyperpolarizability, and γ_{ijkl} are the components of the second dipole hyperpolarizability.

The HF longitudinal static linear polarizability (α_{zz}) and second hyperpolarizability (γ_{ijkl}) was calculated analytically using the Coupled-Hartree–Fock (CPHF)[17] procedure and numerically using the Finite Field Method (FF).[18] At the MP2, CCD, and CCSD levels, the calculation of these properties was performed numerically using the FF method. These molecular properties were obtained from FF calculations using positive and negative field strengths in the range of 0.005 au. Previous studies, based on MP$_2$ calculations, have been reported by showing the importance of the inclusion of electron correlation effects to obtain accurate estimates for the hyper(polarizabilities).[26–28]

TABLE 1: Comparison between the Average CPU Time To Evaluate a Two-Electron Integral of s-Type Using STO-3G and STO-6G Basis Sets and the Equivalent q-Integral, Respectively

basis sets/q-Integral	average CPU time (μs)
STO-6G	666.0938
STO-3G	42.0313
q-Integral	0.3125

All fits performed in this work were obtained using hybrid optimization procedure based on the global optimization method known as Generalized Simulated Annealing (GSA),[29–33] the simplex gradient method,[34] and the Levenberg–Marquardt methods.[35,36] The q-Integral method was implemented in the general ab initio quantum chemistry package GAMESS,[37] where all calculations were performed.

3. Results and Discussion

In this section we compare the results of different electronic and dynamics properties evaluated with the q-Integral and the usual methodology using the MP$_2$ and CC methodologies. The $y_{0_{\mu\nu\lambda\sigma}}$, $\alpha_{\mu\nu\lambda\sigma}$, $\beta_{\mu\nu\lambda\sigma}$, $q_{\mu\nu\lambda\sigma}$, $\gamma_{\mu\nu\lambda\sigma}$, $R_{0_{\mu\nu\lambda\sigma}}$, and $C_{\mu\nu\lambda\sigma}$ are parameters of the q-Morse fit of the symmetric part of the full matrix $\langle\mu\nu|\lambda\sigma\rangle_q$ in terms of the interatomic distance, and were obtained of the reference.[15]

In Table 1 we present the average CPU time (in microseconds) to evaluate the two-electron integral of s-type using STO-3G and STO-6G basis sets and the equivalent q-Integral. In the calculation we used an Intel Q9300 (2.50 GHz) processor. These results show that the q-Integral method is about 134.5 (2131.5) times faster when compared to the CPU time of calculation using the STO-3G(STO-6G) basis sets to calculate the two-electron integrals. It is important to point out that the CPU time reduction is more significant when larger molecular systems and basis sets are employed. For this comparison we used also a FORTRAN ab initio computational code developed and optimized in our research group.

Figure 1a shows the H$_2$ PECs using the STO-6G basis set and corresponding q-Integrals (q-STO-6G integrals) as well as the H$_2$ PECs using the DZV basis set and the corresponding q-Integrals (q-DZV integrals) calculated using the MP$_2$ perturbation theory. Figure 1b,c present the PECs using the STO-6G and DZV basis sets and corresponding q-STO-6G and q-DZV integrals calculated using the CCD and CCSD approaches of CC theory, respectively. From these figures, one can see a good agreement between the q-PECs and the PECs calculated at different theory levels by using the $\langle\mu\nu|\lambda\sigma\rangle_q$ and the $\langle\mu\nu|\lambda\sigma\rangle$, respectively. To avoid the proliferation of the figures only STO-6G and DZV PECs were included in Figure 1.

In Table 2, we present the results of the maximum and minimum deviation and the χ^2 error between the calculation of PECs and q-PECs obtained by the HF, MP$_2$, CCD, and CCSD theory levels using the STO-3G, STO-6G, and DZV basis set functions and their respective q-Integrals. Note that the same tendency for error found in the HF approach is verified when the correlation corrections to the SCF wave function are performed.

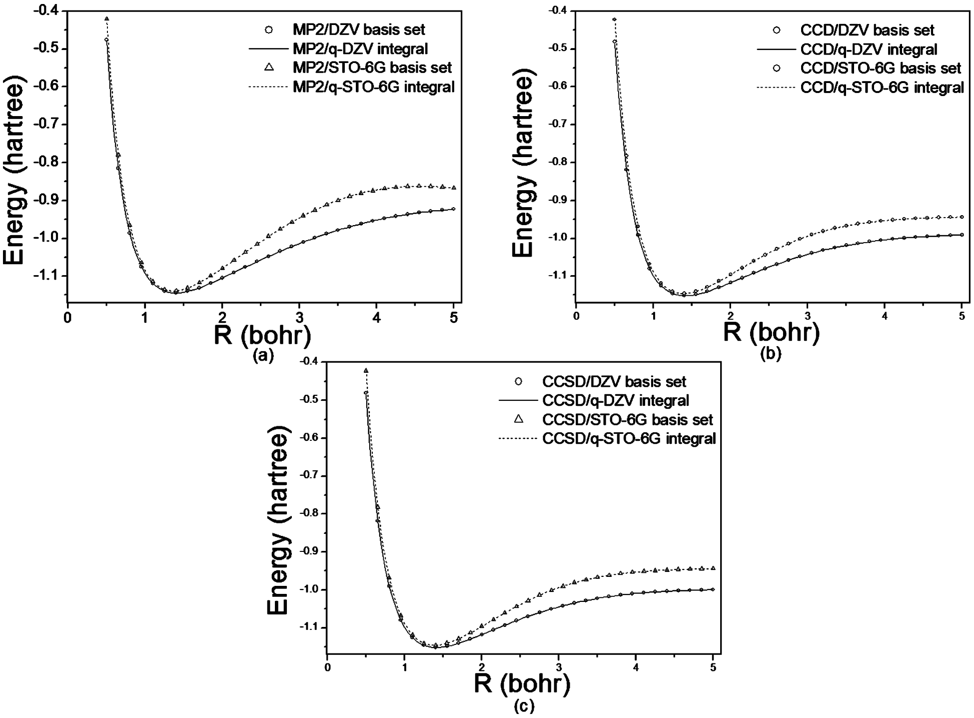

Figure 1. Comparison between DZV PEC (circle), q-DZV PEC (solid line), STO-6G PEC (triangle), and q-STO-6G (dashed line) using (a) MP_2, (b) CCD, and (c) CCSD levels.

TABLE 2: Maximum, Minimum, and χ^2 Errors between the PEC and the Respective q-PEC Obtained by HF, MP_2, CCD, and CCSD Levels

	STO-3G/q-STO-3G			STO-6G/q-STO-6G			DZV/q-DZV		
level	max error	min error	χ^2 error	max error	min error	χ^2 error	max error	min error	χ^2 error
HF[a]	7.7×10^{-5}	5.2×10^{-8}	1.2×10^{-9}	3.5×10^{-5}	1.9×10^{-7}	2.6×10^{-10}	1.5×10^{-5}	2.2×10^{-7}	2.5×10^{-11}
MP_2	9.0×10^{-5}	2.4×10^{-7}	1.4×10^{-9}	1.3×10^{-4}	0.0000	1.1×10^{-9}	3.0×10^{-5}	0.0000	4.3×10^{-11}
CCD	6.6×10^{-5}	8.9×10^{-7}	9.6×10^{-10}	2.1×10^{-5}	9.5×10^{-7}	1.4×10^{-10}	4.3×10^{-4}	0.0000	1.2×10^{-10}
CCSD	6.6×10^{-5}	1.2×10^{-7}	1.0×10^{-9}	2.1×10^{-5}	9.5×10^{-7}	1.4×10^{-10}	5.0×10^{-4}	0.0000	1.1×10^{-10}

[a] Results obtained from ref 15.

TABLE 3: Optimized Equilibrium Distance of the H_2 System Obtained by HF, MP_2, CCD, and CCSD Methods

level	STO-3G	q-STO-3G	STO-6G	q-STO-6G	DZV	q-DZV
HF	1.345917	1.345918	1.342678	1.342680	1.379177	1.379186
MP_2	1.367743	1.367744	1.364378	1.364379	1.393214	1.393225
CCD	1.388808	1.389549	1.385283	1.385275	1.408609	1.408881
CCSD	1.388808	1.389549	1.385283	1.385275	1.409631	1.409910

Table 3 shows the interatomic equilibrium distance of the H_2 system using the STO-3G, STO-6G, and DZV basis sets and corresponding q-Integrals calculated at the MP_2, CCD, and CCSD levels. The maximum (minimum) percent deviations found between values for the equilibrium distance were 6.5×10^{-6}% (7.4×10^{-5}%) at the HF level, 7.9×10^{-4}% (7.3×10^{-5}%) at the MP2 level, and 5.3×10^{-2}% (5.8×10^{-4}%) at both the CCD and CCSD levels.

Table 4 lists a set of rovibrational transitions using both the PECs and the q-PECs for the different basis sets. The maximum (minimum) difference between the PECs and the equivalent q-PECs rovibrational spectra ($\Delta E_{(\nu-\nu',J)} = E_{(\nu-\nu',J)}(\text{PEC}) - E_{(\nu-\nu',J)}(q\text{−PEC})$) considering all the calculated rovibrational levels ($J = 0,1$ and $\nu = 0, 1, 2, 3$) is $\Delta E_{(0-1,J=1)} = 3.72$ cm^{-1} ($\Delta E_{(0-1,J=0)} = 1.23$ cm^{-1}) for the HF/STO-3G level; $\Delta E_{(0-1,J=1)} = 3.72$ cm^{-1} ($\Delta E_{(0-1,J=0)} = 1.23$ cm^{-1}) for the HF/STO-6G level and $\Delta E_{(0-3,J=0,1)} = 0.70$ cm^{-1} ($\Delta E_{(0-1,J=0,1)} = 0.23$ cm^{-1}) for the HF/DZV level; $\Delta E_{(0-3,J=1)} = 4.76$ cm^{-1} ($\Delta E_{(0-1,J=1)} = 0.44$ cm^{-1}) for the MP_2/STO-3G level; $\Delta E_{(0-3,J=0)} = 0.55$ cm^{-1} ($\Delta E_{(0-1,J=1)} = 0.44$ cm^{-1}) for the MP_2/STO-6G level; and $\Delta E_{(0-3,J=0)} = 2.62$ cm^{-1} ($\Delta E_{(0-1,J=0)} = 1.76$ cm^{-1}) for the MP_2/DZV level; $\Delta E_{(0-3,J=1)} = 6.48$ cm^{-1} ($\Delta E_{(0-1,J=0)} = 0.73$ cm^{-1}) for the CCD/STO-3G level; $\Delta E_{(0-3,J=0,1)} = 2.21$ cm^{-1} ($\Delta E_{(0-1,J=0,1)} = 0.69$ cm^{-1}) for the CCD/STO-6G level and $\Delta E_{(0-2,J=0)} = 1.51$ cm^{-1} ($\Delta E_{(0-3,J=1)} = 1.18$ cm^{-1}) for the CCD/DZV level; $\Delta E_{(0-1,J=1)} = 7.69$ cm^{-1} ($\Delta E_{(0-1,J=0)} = 1.16$ cm^{-1}) for the CCSD/STO-3G level; $\Delta E_{(0-3,J=0)} = 2.28$ cm^{-1} ($\Delta E_{(0-1,J=1)} = 0.49$ cm^{-1}) for the CCSD/STO-6G level and $\Delta E_{(0-2,J=0)} = 1.46$ cm^{-1} ($\Delta E_{(0-3,J=1)} = 0.99$ cm^{-1}) for the CCSD/DZV level. These results indicate that the difference between the PEC and the corresponding q-PEC rovibrational spectra decrease when high-quality basis set functions are used.

The PECs and the q-PECs spectroscopic constants obtained through the Dunham method and nuclear Schrödinger solutions are shown in Tables 5 and 6, respectively. The percent deviations found between the PEC and q-PEC values for the rotational constant (B_e) using the Dunham method were 0.00% for all basis sets employed in this work at the HF and MP_2 level. At the CCD (CCSD) level these deviations were: 0.097% (0.097%), 0.00% (0.00%), and 0.02% (0.03%) for the STO-3G, STO-6G,

TABLE 4: H_2 Rovibrational Spectra (cm^{-1}) for Different Basis Sets and the Respective PECs and q-PECs Obtained by the HF, MP_2, CCD, and CCSD Methods

			rovibrational spectra					
level	ν	J	STO-3G	q-STO-3G	STO-6G	q-STO-6G	DZV	q-DZV
HF[a]	$0 \rightarrow 1$	0	5290.48	5291.71	5319.97	5320.20	4414.47	4414.12
	$0 \rightarrow 2$		10413.17	10415.35	10472.49	10472.99	8613.36	8613.23
	$0 \rightarrow 3$		15379.29	15382.90	15464.29	15464.99	12611.57	12612.03
	$0 \rightarrow 1$		5286.71	5287.98	5316.35	5316.58	4408.61	4408.27
	$0 \rightarrow 2$	1	10405.89	10408.14	10465.37	10465.87	8601.98	8601.85
	$0 \rightarrow 3$		15368.70	15372.42	15453.79	15454.49	12594.98	12595.43
MP_2	$0 \rightarrow 1$	0	5058.79	5058.27	5089.26	5089.39	4306.60	4304.82
	$0 \rightarrow 2$		9962.79	9964.34	10027.68	10028.04	8406.26	8403.79
	$0 \rightarrow 3$		14738.36	14742.97	14834.46	14835.01	12318.64	12316.02
	$0 \rightarrow 1$	1	5053.83	5053.39	5084.40	5084.53	4300.07	4298.31
	$0 \rightarrow 2$		9952.11	9953.80	10016.97	10017.33	8392.67	8390.24
	$0 \rightarrow 3$		14721.12	14725.88	14816.93	14817.47	12297.58	12295.00
CCD	$0 \rightarrow 1$	0	4776.79	4777.52	4806.41	4807.10	4119.86	4118.56
	$0 \rightarrow 2$		9350.61	9354.01	9409.53	9411.03	7992.77	7991.26
	$0 \rightarrow 3$		13735.82	13742.18	13817.21	13819.42	11632.79	11631.56
	$0 \rightarrow 1$	1	4771.33	4772.14	4801.05	4801.74	4112.82	4111.55
	$0 \rightarrow 2$		9339.09	9342.61	9397.96	9399.47	7978.23	7976.77
	$0 \rightarrow 3$		13717.49	13723.97	13798.55	13800.76	11610.44	11609.26
CCSD	$0 \rightarrow 1$	0	4776.49	4777.65	4806.64	4807.13	4100.40	4101.71
	$0 \rightarrow 2$		9350.09	9354.32	9410.00	9411.36	7949.62	7951.08
	$0 \rightarrow 3$		13735.16	13742.73	13817.94	13820.22	11559.89	11560.92
	$0 \rightarrow 1$	1	4771.02	4772.26	4801.27	4801.76	4093.31	4094.59
	$0 \rightarrow 2$		9338.57	9342.92	9398.43	9399.78	7934.96	7936.37
	$0 \rightarrow 3$		13716.83	13724.52	13799.28	13801.54	11537.33	11538.32

[a] Results obtained from ref 15.

TABLE 5: H_2 Rovibrational Spectroscopic Constants (cm^{-1}) Obtained with the Dunham Method for PECs and q-PECs Using the HF, MP_2, CCD, and CCSD Methods

level		STO-3G	q-STO-3G	STO-6G	q-STO-6G	DZV	q-DZV
HF[a]	B_e	65.94	65.94	66.25	66.25	62.79	62.79
	ω_e	5443.95	5444.47	5431.69	5430.35	4480.50	4481.21
	$\omega_e x_e$	99.61	96.81	89.69	89.58	121.10	120.80
	α_e	2.076	2.023	1.894	1.894	3.009	2.999
MP_2	B_e	63.85	63.85	64.16	64.16	61.53	61.53
	ω_e	5243.68	5246.06	5261.54	5261.56	4532.79	4530.94
	$\omega_e x_e$	108.63	105.54	99.74	99.83	125.35	124.11
	α_e	2.282	2.221	2.097	2.102	3.073	3.052
CCD	B_e	61.92	61.86	62.24	62.24	60.17	60.18
	ω_e	4998.00	4995.27	5019.82	5019.96	4375.75	4379.04
	$\omega_e x_e$	120.64	118.13	114.52	114.30	138.18	139.33
	α_e	2.585	2.529	2.398	2.396	3.327	3.352
CCSD	B_e	61.92	61.86	62.24	62.24	60.11	60.09
	ω_e	5000.23	4995.17	5019.58	5019.85	4365.24	4364.36
	$\omega_e x_e$	121.04	118.08	114.37	114.16	140.33	142.07
	α_e	2.554	2.529	2.397	2.395	3.351	3.378

[a] Results obtained from ref 15.

TABLE 6: H_2 Rovibrational Spectroscopic Constants (cm^{-1}) Obtained with Solution of the Nuclear Schrödinger Equation for PECs and q-PECs Using the HF, MP_2, CCD, and CCSD Methods

level		STO-3G	q-STO-3G	STO-6G	q-STO-6G	DZV	q-DZV
HF[a]	ω_e	5464.93	5467.25	5490.11	5490.21	4638.14	4637.06
	$\omega_e x_e$	92.13	92.87	88.70	88.61	118.79	118.38
	$\omega_e y_e$	1.86	1.99	1.12	1.10	2.48	2.45
	α_e	2.016	1.998	1.878	1.779	3.088	3.081
MP_2	ω_e	5234.57	5230.00	5254.66	5254.55	4526.48	4523.11
	$\omega_e x_e$	97.49	94.98	90.34	90.18	118.56	117.60
	$\omega_e y_e$	4.38	4.11	3.20	3.18	3.29	3.20
	α_e	2.109	2.047	1.930	1.934	3.005	2.987
CCD	ω_e	4988.49	4985.82	5012.66	5012.99	4373.82	4370.92
	$\omega_e x_e$	112.42	110.24	107.92	107.68	134.35	133.37
	$\omega_e y_e$	2.36	2.09	1.30	1.26	2.36	2.27
	α_e	2.438	2.380	2.267	1.984	3.293	3.268
CCSD	ω_e	4988.09	4985.91	5012.85	5012.65	4356.84	4359.84
	$\omega_e x_e$	112.38	110.22	107.90	107.47	135.12	136.14
	$\omega_e y_e$	2.36	2.09	1.30	1.24	2.06	2.16
	α_e	2.437	2.380	2.269	2.265	3.305	3.330

[a] Results obtained from ref 15.

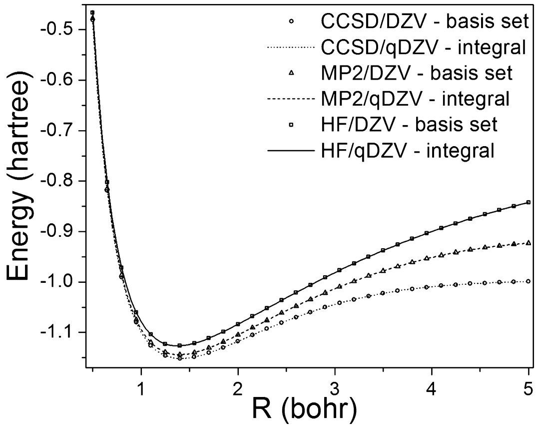

Figure 2. Comparison between the PECs using STO-3G (dashed line), STO-6G (dotted line), and DZV (circle) basis sets and the PEC using the q-Integral (solid line) obtained from the DZV basis set.

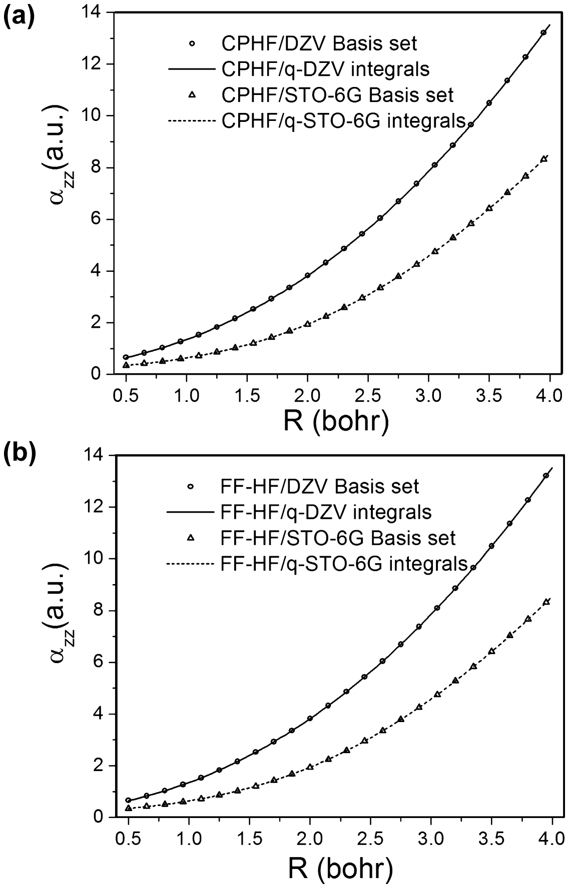

Figure 3. Bond length dependence of the longitudinal static linear polarizability calculated using STO-6G (triangle line), q-STO-6G (solid line), DZV (circle), and q-DZV (solid line) obtained by (a) CPHF and (b) FF calculations.

and DZV basis sets, respectively. For the equilibrium vibrational frequency (ω_e) using the Dunham method these percent deviations were 0.045% for the STO-3G basis, 0.00038% for the STO-6G basis and 0.040% for the DZV basis at MP_2 level. Still, for the ω_e constant, at level CCD (CCSD) these percent deviations were 0.054% (0.10%), 0.0028% (0.0054%), and 0.075% (0.020%) for the STO-3G, STO-6G, and DZV basis sets, respectively. For the first anharmonic constant ($\omega_e x_e$) and the vibration−rotation coupling constant (α_e), these percents deviations were 2.84% and 2.67% (STO-3G basis), 0.09% and 0.24% (STO-6G basis), and 0.98% and 0.68% (DZV basis) at the MP_2 level and 2.08% and 2.17% (STO-3G basis), 0.19% and 0.083% (STO-6G basis), and 0.83% and 0.75% (DZV basis) at the CCD level, and 2.44% and 0.98% (STO-3G basis), 0.18% and 0.083% (STO-6G basis), and 1.24% and 0.80% (DZV basis) at the CCSD level. On the other hand, when we used the nuclear Schrödinger equation, the following percents deviations were observed for ω_e, $\omega_e x_e$, $\omega_e y_e$ (the second anharmonic constant), and α_e, respectively: 0.087%, 2.57%, 6.16%, 2.94% (STO-3G), 0.0021%, 0.18%, 0.62%, 0.21% (STO-6G), and 0.074%, 0.81%, 2,74%, 0.60% at (DZV) basis at the MP_2 level; 0.053%, 1.94%, 11.44%, 2.38% (STO-3G), 0.0066%, 0.22%, 3.08%, 12.48% (STO-6G), and 0.066%, 0.72%, 3.81%, 0.76% at (DZV) basis at the CCD level. The same tendency is verified for the CCSD level, and therefore it was omitted to avoid the proliferation of number.

Although the deviations are small, it is important to mention that, even when a q-BO polynomial form[17] of the tenth degree is used, we can still have a slight (χ^2) accuracy problem in the electronic energy fit procedure. This means that part of the discrepancy between the PECs may be due not only to the q-Integrals but also to the quality of the electronic energy fit.

Figure 2 shows a comparison of the DZV PECs with the q-PECs obtained using q-DZV integral at the HF, MP_2, and CCSD levels. From these figures, we can see a good agreement between q-PECs and the PECs calculated at different theory levels. From all basis sets and levels of theory considered in this work the CCSD/DZV and CCSD/q-DZV are the ones that best describe the H_2 potential energy curve, as expected, indicating that the small deviation between the q-Integral and standard methods to solve the two-electron integral does not compromise the superiority of DZV PEC in comparison to the PEC obtained using the *single*-ζ basis sets.

Parts a and b of Figure 3 show the bond length dependence of the longitudinal static polarizability using the STO-6G and DZV basis sets and their respective q-Integrals. In Figure 3a, the linear polarizability was calculated analytically using the CPHF procedure, and in Figure 3b it was calculated numerically using the FF method. The maximum and minimum deviation and the χ^2 error between the bond length dependence of linear polarizability using the q-Integral method and the usual one are shown in Table 7.

In Figure 4a,b we show the length dependence of the longitudinal static second hyperpolarizability of the H_2 calculated

TABLE 7: Maximum, Minimum, and χ^2 Errors Found for Bond Length Dependence of the Longitudinal Static Linear Polarizability Obtained by Different Methodologies

	STO-3G/q-STO-3G			STO-6G/q-STO-6G			DZV/q-DZV		
level	max error	min error	χ^2 error	max error	min error	χ^2 error	max error	min error	χ^2 error
CPHF	4.3×10^{-4}	6.8×10^{-7}	7.3×10^{-7}	1.1×10^{-4}	4.8×10^{-7}	2.5×10^{-7}	3.3×10^{-4}	4.3×10^{-6}	4.9×10^{-7}
FF-HF	3.9×10^{-4}	6.3×10^{-7}	6.6×10^{-7}	1.1×10^{-4}	4.8×10^{-7}	2.5×10^{-7}	3.3×10^{-4}	4.3×10^{-6}	4.9×10^{-7}
FF-MP_2	8.8×10^{-4}	1.4×10^{-7}	6.6×10^{-7}	8.8×10^{-4}	1.4×10^{-7}	6.6×10^{-7}	9.5×10^{-4}	9.1×10^{-6}	3.0×10^{-7}
FF-CCD	2.1×10^{-3}	1.1×10^{-5}	1.0×10^{-5}	2.1×10^{-3}	1.1×10^{-5}	1.0×10^{-5}	9.2×10^{-4}	4.6×10^{-5}	8.9×10^{-6}
FF-CCSD	2.0×10^{-3}	3.3×10^{-5}	2.6×10^{-5}	2.0×10^{-3}	3.3×10^{-5}	2.6×10^{-5}	9.4×10^{-4}	2.8×10^{-5}	6.1×10^{-6}

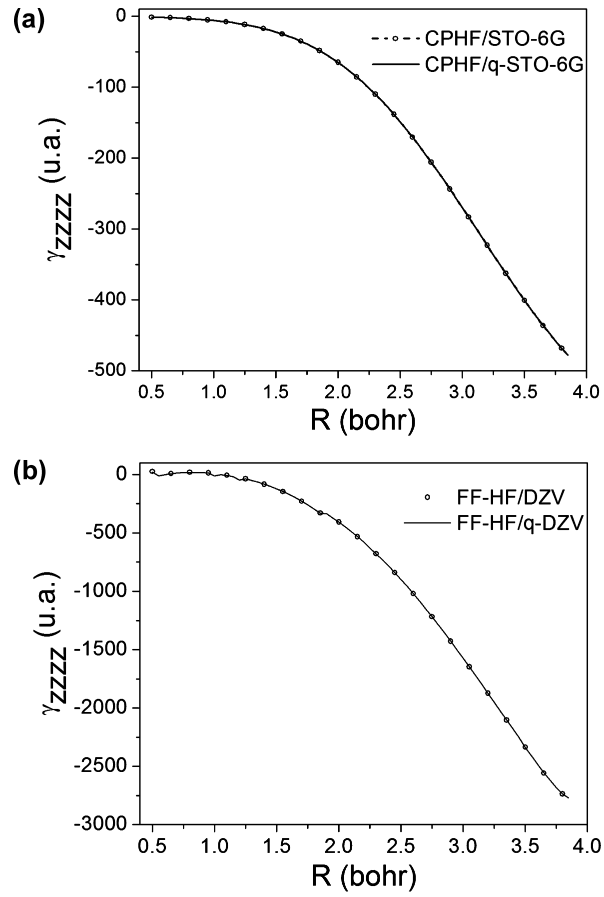

Figure 4. Bond length dependence of the longitudinal static second hyperpolarizability calculated using STO-6G (circle line) and q-STO-6G (solid line) obtained by (a) CPHF and (b) FF calculations.

analytically using the CPHF procedure and numerically using the FF method, respectively. In both cases, the DZV basis sets and your respectively q-DZV integrals were employed. For these cases, the maximum (minimum) and χ^2 errors between the bond length dependence of second hyperpolarizability using the q-Integral method and usual one were 4.5×10^{-3} (6.7×10^{-6}) and 4.9×10^{-7} au at the FF-HF/DZV(q-DZV) level and 2.1×10^{-4} (2.8×10^{-7}) and 4.7×10^{-7} au at the CPHF/STO-6G(q-STO-6G) level.

All calculations described in this work were performed using the general ab initio quantum chemistry package GAMESS.

4. Conclusions

In this paper we have investigated the accuracy of q-Integrals as a function of the internuclear distance for H_2 molecular systems through some levels of calculations with inclusion of the EC effects. To this end, we employed the q-Integral method to construct the potential energy curve for the H_2 molecule and used the PEC to determine rovibrational levels and spectroscopic constants of the molecule, which are properties that are very sensitive to the form of the PEC. Furthermore, we determined the bond length dependence of the longitudinal static linear polarizability and second longitudinal hyperpolarizability and optimized the interatomic distance for the related molecular system. Our main conclusions follow:

1. There is a reasonable difference in the computational effort to rate the matrix of the two-electron ($\langle \mu\nu | \lambda\sigma \rangle$) between both usual and q-Integral methods. While the methodology requires, formally, the calculation of $N^4 \times L^4$ integrals of the kind $\langle pq|st \rangle$, for the q-Integral method it is necessary to evaluate only N^4 integrals $\langle pq|st \rangle$. In this case N and L are the number of base functions and the number of contracted Gaussians functions used to expand the atomic orbital, respectively.

2. Comparing the calculations of two-electron integrals of the basic functions of the type contracted STO-LG, using the ordinary method and the q-Integrals, it is clear that our procedure is particularly more advantageous the greater the size of the contraction.

3. The rovibrational levels and the spectroscopic constants obtained with q-Integrals are in very close agreement with the ones obtained through the standard procedure for calculating the two-electron integrals. The same tendency is verified to calculate longitudinal static longitudinal hyper(polarizability) as well as optimized internuclear distances. Moreover, as the quality of the basis set increases, so do the calculated spectroscopic constants using either standard (DZV) or q-Integral (q-DZV) procedures.

4. The feasibility of using the q-Integral method opens the perspective of applying it in calculations of large molecular systems that, in the context of the current methods, are prohibitive.

5. The results obtained clearly indicate that the q-Integral method is accurate enough to be used in any molecular quantum mechanical calculation.

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