The effect of 1s correlation on D_e, r_e, and ω_e of first-row diatomics

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Advances in the continuing development of quantitatively accurate *ab initio* methods have revealed the necessity of a full understanding of the consequences of core electron correlation on molecular properties.[1–3] Bauschlicher and Partridge (BP)[1] have recently reported a concerted *ab initio* investigation of $1s$ correlation effects on the dissociation energy (D_e), equilibrium bond length (r_e), and harmonic vibrational frequency (ω_e) of N_2. Some key conclusions of the study were as follows: (1) The $1s$ correlation effect on $D_e(N_2)$ diminishes to about $+0.8$ kcal mol^{-1} once size-extensive methods are employed. (2) The equilibrium bond distance of N_2 experiences a 0.002 Å contraction, reducing the errors in r_e to less than 0.001 Å. (3) The total change in the harmonic frequency due to $1s$ correlation is $+9$ cm^{-1}, a shift engendering a $+8.4$ cm^{-1} error in the CCSD(T) prediction, which was previously found[4] to be virtually coincident with experiment.

The manifestations of $1s$ correlation on the spectroscopic constants of diatomics involving first-row atoms have been probed more broadly in recent work in our laboratories. In Table I appears a collection of CCSD(T) results[5] for N_2, O_2, F_2, CO, NO, and HF obtained with correlation-consistent basis sets[6,7] similar to those employed by BP. Salient is the performance of the core-correlated CV(QZ) CCSD(T) method in predicting equilibrium distances with a mean error of only 0.0009 Å. The effects of $1s$ correlation on $[D_e(\text{kcal mol}^{-1}), r_e(\text{Å})]$ are $N_2(+0.78,-0.0021)$, $O_2(+0.24,-0.0020)$, $F_2(-0.09,-0.0014)$, CO$(+0.93,-0.0024)$, NO$(+0.42,-0.0021)$, and HF$(+0.18,-0.0006)$, the general trends among which are transparent *vis-à-vis* the associated bond energies and equilibrium distances. Nonetheless, the F_2 molecule appears to be a peculiar system in which $1s$ correlation actually decreases the atomization energy.

The consequences of $1s$ correlation on the diatomic ω_e values are subtle, requiring a partitioning of competing factors for a perspicacity of observed data trends. Our computations at indisputably high levels of theory reveal that $1s$ correlation furnishes a correction function to the valence diatomic potential energy curve which has *negative* curvature at all bond lengths in the vicinity of the equilibrium position. That the total, phenomenological $1s$ correlation shift on ω_e is usually observed to be positive[1,4] demands explanation. Our resolution of this problem entails quantifying the interplay of curvature reduction (the *direct* effect) with equilibrium bond-length contraction (the *indirect* effect).

The suggested partitioning of $1s$ correlation effects is elucidated in Fig. 1, where separate CCSD(T) data obtained with the CV basis of BP are employed to expose the variation of the quadratic force constant with internuclear distance in the N_2 example. Two reference bond lengths of N_2 are considered, $r_A=1.0978$ Å and $r_B=1.0999$ Å, viz., the equilibrium bond lengths[1] given respectively by the CV CCSD(T) full (14-e) and frozen-core (10-e) levels of theory. The r_A value is equivalent to the empirical r_e distance within 0.000 12 Å. The second derivative of the diatomic potential energy function can be evaluated at each reference bond length at both the 14-e and 10-e CV CCSD(T) levels and compared to experimental results derived from our previous analysis of the RKR data of N_2.[8] To each quadratic force constant $f_{rr}(r)$, a harmonic frequency $\omega(r)$ can then be ascribed by means of the standard formula, whether or not the point of reference is the equilibrium geometry of the associated potential curve.

The series of $\omega(r)$ curves allows the *indirect* manifestations of reference geometry shifts to be isolated from the *direct* effects of electron correlation and basis set incompleteness. While the 10-e CV CCSD(T) result for $\omega_e=\omega(r=1.0999$ Å$)$ agrees with the experimental quantity (2357.6 cm^{-1}) within 0.4 cm^{-1}, the analogous $\omega(r)$ prediction at 1.0978 Å is 17.5 cm^{-1} too high. The inclusion of $1s$ correlation under the constraint of *fixed* internuclear distance actually decreases the quadratic force constant such that the frequency is *lowered* by about 8.1 cm^{-1}. Hence, a 14-e CCSD(T) treatment with a reasonably complete basis set yields a prediction for $\omega_e=\omega(r=1.0978$ Å$)$ which is still too large, but only by 9.4 cm^{-1}. In brief, the inner-shell, curvature-reduction effect works to diminish the valence level overshoot by 50% for an internuclear distance fixed at the experimental r_e value. Nevertheless, if the total $1s$ correlation effect is considered in a conventional, phenomenological sense as the difference between the $\omega(r)$ values for 10-e CV(QZ) CCSD(T) at 1.0999 Å vs 14-e CV(QZ) CCSD(T) at 1.0978 Å, then $1s$ correlation can be said to *increase* the harmonic frequency by 9.8 cm^{-1}, in accord with the direction of the shift usually anticipated from the associated changes in r_e and D_e.

The analysis of Fig. 1 explicates our previous observation[3,8] that the valence CCSD(T) method implemented with a basis set of $[5s4p3d2f1g]$ quality containing no core polarization overshoots the exact quadratic force constant of N_2 at the true r_e distance by an amount corresponding to a 19 cm^{-1} error in $\omega(r)$. It is thus apparent that the exceptional accuracy of an earlier ANO CCSD(T) result[4] for ω_e is in part attributable to a particularly advantageous cancellation of reference geometry overestimation and direct deficiencies in the correlation treatment. The harmonic frequency data in Table I demonstrate the regularity of this occurrence for first-row diatomics, and arguably its utility as a computational artifice. All $\omega(r)$ entries therein involve fixed, experimental reference geometries ($r_e^{\rm EXPT}$), in order to isolate the competing effects of concern. The valence CV(QZ) CCSD(T) quadratic force constants at the true equilibrium structures overestimate the harmonic frequency by 0.6%–0.8% and 1.0%–1.4%, respectively, for the closed- and open-shell species involving two heavy atoms. The *direct* inclusion of 1*s* correlation changes $\omega(r_e^{\rm EXPT})$ for (N_2,O_2,F_2,CO,NO) by $(-8.1,-5.7,-3.2,-8.5,-6.7)$ cm^{-1}, in order, which reduces the observed discrepancy by 0.3%–0.4% in each case. A conventional frozen-core cc-pVQZ CCSD(T) determination of ω_e at the corresponding theoretical equilibrium geometry happens to circumvent much of the inherent frequency error for these molecules, especially the closed-shell species, due to the interplay of the $+0.002$ Å

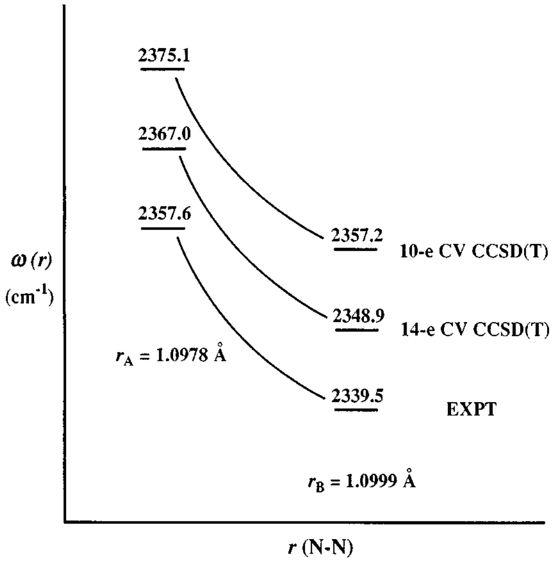

FIG. 1. A schematic representation of the functional dependence of harmonic frequency predictions of N_2 on the internuclear separation. The $\omega(r_A)$ values are 1.0 cm^{-1} lower than the analogous entries in Table I primarily because $r_A - r_e = +0.000\,115$Å.

TABLE I. Theoretical and experimental molecular constants for selected first-row diatomics.[a,b]

	CCSD(T)					
	cc-pVTZ	CV(TZ)	cc-pVQZ	CV(QZ)	pVPZ	EXPT[c]
$N_2(X\,^1\Sigma_g^+)$						
D_e	216.4	219.57 (220.35)	222.9	223.35 (224.13)	224.3	228.4
r_e	1.1038	1.0993 (1.0973)	1.1003	1.0999 (1.0978)	1.0994	1.0977
$\omega(r_e^{\rm EXPT})$	2398.2	2371.0 (2363.2)	2378.4	2376.1 (2368.0)	2372.8	2358.6
$O_2(X\,^3\Sigma_g^-)$						
D_e	99.7	114.64 (114.89)	117.2	117.41 (117.65)	117.9	120.2
r_e	1.2118	1.2096 (1.2077)	1.2076	1.2071 (1.2051)	1.2075	1.2074
$\omega(r_e^{\rm EXPT})$	1612.7	1599.5 (1593.9)	1602.7	1602.1 (1596.4)	1599.1	1580.2
$F_2(X\,^1\Sigma_g^+)$						
D_e	34.8	35.43 (35.35)	36.7	36.79 (36.70)	37.3	38.2
r_e	1.4158	1.4133 (1.4119)	1.4129	1.4126 (1.4112)	1.4124	1.4119
$\omega(r_e^{\rm EXPT})$	933.1	931.5 (928.3)	924.5	923.3 (920.1)	925.3	916.6
$CO(X\,^1\Sigma^+)$						
D_e	244.7	254.41 (255.34)	256.1	256.37 (257.30)	256.7	258.9
r_e	1.1357	1.1302 (1.1279)	1.1314	1.1309 (1.1285)	1.1308	1.1283
$\omega(r_e^{\rm EXPT})$	2210.3	2178.5 (2170.3)	2187.9	2184.0 (2175.5)	2182.9	2169.8
$NO(X\,^2\Pi)$						
D_e	130.2	145.33 (145.76)	148.4	148.77 (149.19)	149.4	152.5
r_e	1.1565	1.1527 (1.1507)	1.1528	1.1525 (1.1504)	1.1522	1.1508
$\omega(r_e^{\rm EXPT})$	1943.4	1916.5 (1910.0)	1925.4	1923.9 (1917.2)	1917.4	1904.2
$HF(X\,^1\Sigma^+)$						
D_e	137.0	137.81 (138.00)	140.0	140.03 (140.21)	140.9	141.2
r_e	0.9172	0.9134 (0.9128)	0.9162	0.9159 (0.9153)	0.9163	0.9168
$\omega(r_e^{\rm EXPT})$	4184.0	4122.8 (4118.6)	4153.3	4148.2 (4143.7)	4146.8	4138.3

[a] Units: D_e (kcal mol^{-1}), r_e (Å), and ω (cm^{-1}). Primary data entries from valence-shell treatments only, whereas results in parentheses include the effects of 1*s* core correlation.

[b] The harmonic frequencies $\omega(r)$ are evaluated from quadratic force constants computed at the precise experimental equilibrium distances ($r_e^{\rm EXPT}$), thus exposing the direct effects of 1*s* correlation. The indirect 1*s* effects due to bond-length contraction can be gauged from the following true CV(QZ) CCSD(T) ω_e values calculated at the respective optimized distances: N_2 [2357.1(2366.9)], O_2[1603.9(1609.6)], F_2[921.0(922.6)], CO[2164.6(2174.4)], NO[1911.8(1919.7)], and HF[4161.7(4166.3)].

[c] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

disparity in r_e and the magnitude of the associated cubic force constant for bond elongation.[9] For HF the trends are the same, albeit proportionately diminished, the direct 1s effect on the harmonic frequency being $-4.5\ \text{cm}^{-1}$, which roughly halves the 0.2% error in $\omega(r_e^{\text{EXPT}})$ found at the valence CV(QZ) CCSD(T) level.

In summary, a collection of high-level D_e, r_e, and ω_e data for first-row diatomics is presented here which more broadly substantiates the effects of 1s correlation on molecular properties. Partitionings similar to that applied for harmonic frequencies can be cogently constructed for other spectroscopic parameters such as D_e and $\omega_e x_e$, but in the former case the indirect effects are insignificant, consistently less than 0.01 kcal mol^{-1}. Whether the consequences of core correlation for first-row diatomics are characteristic of those for a wide range of heavier systems remains to be demonstrated.

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[5] All computations reported here were carried out with the program package PSI 2.0. No spherical symmetry restrictions were invoked for the atoms. Open-shell CCSD(T) energies were determined from RHF orbitals as described in G. E. Scuseria, Chem. Phys. Lett. **176**, 27 (1991). All molecular constants were obtained from higher-order central difference formulas, as applied to tightly converged (10^{-11} a.u.) energy points computed at r_e^{EXPT} and geometries displaced by ±0.01 Å and ±0.02 Å therefrom.

[6] The basis sets denoted as cc-pVTZ and cc-pVQZ are exactly those of Dunning *et al.* (Ref. 7), whereas the pVPZ set was obtained from the corresponding cc-pV5Z basis by deleting the h manifold. The CV(TZ) and CV(QZ) basis sets, designed to recover the effects of 1s correlation, were constructed from their cc-pVTZ and cc-pVQZ counterparts by completely uncontracting the sp space and adding two tight d and f sets via extension of the polarization manifolds into the core region with a geometric ratio of 3.0.

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[9] For small reference bond-length variations (δ_r), it can be shown that the percentage change (p_ω) in the predicted harmonic frequency at a given level of theory is approximately $50\rho\delta_r$, where $\rho = f_{rrr}/f_{rr}$ is the ratio of the quadratic to cubic force constant near equilibrium. For the molecules in Table I, $\rho \in [-7.17, -7.80]$ Å^{-1}, and thus a $\delta_r \approx 0.002$ Å error due to neglect of 1s correlation gives rise to $p_\omega \approx -0.75\%$.