Intracule functional models. IV. Basis set effects

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We have calculated position and dot intracules for a series of atomic and molecular systems, starting from an unrestricted Hartree–Fock wave function, expanded using the STO-3G, 6–31G, 6–311G, 6-311++G, 6-311++G(d,p), 6-311++G($3d,3p$), and 6-311++G($3df,3pd$) basis sets as well as the nonpolarized part of Dunning's cc-pV5Z basis. We find that the basis set effects on the intracules are small and that correlation energies from the dot intracule ansatz are remarkably insensitive to the basis set quality. Mean absolute errors in correlation energies across the G1 data set agree to within 2 mE_h for all basis sets tested. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3122422]

I. INTRODUCTION

In the context of quantum chemistry, intracules are two-electron distribution functions that contain information about quantities such as the distance $u=|\boldsymbol{r}_1-\boldsymbol{r}_2|$ between two electrons or their relative momentum $v=|\boldsymbol{p}_1-\boldsymbol{p}_2|$. The position intracule $P(u)$, for example, gives the probability of finding two electrons separated by a relative distance u.[1–4] Likewise, the momentum intracule, $M(v)$, gives the probability of finding two electrons moving with relative momentum v.[5,6]

As functions that contain explicit two-electron information, it is natural to ask whether $P(u)$ and/or $M(v)$ provide a suitable foundation for the construction of post-Hartree–Fock (HF) correlation energy models. Unfortunately, it appears that neither is ideal for the prediction of the electron correlation energy, E_c, as illustrated by the isoelectronic series of heliumlike ions[7] where, as the nuclear charge Z increases, one finds that $\langle u \rangle$ decreases as $O(Z^{-1})$, $\langle v \rangle$ increases as $O(Z)$, and E_c approaches a constant. This suggests that the product variable $s=uv$ may be the smallest basic unit required to model correlation energies and implies that an intracule-based correlation model containing information about both u and v is required for accurate correlation energies.

The Uncertainty Principle precludes the construction of a joint probability density in position and momentum space but we have managed nonetheless to generate phase-space intracules from the second-order reduced Wigner distribution,[8,9] a joint quasiprobability for the two-electron position-momentum density. In this way, we have constructed the Omega intracule $\Omega(u,v,\omega)$[10,11] which can be interpreted as the joint quasiprobability density for u, v, and ω, the latter being the angle between the interelectronic distance vectors $\boldsymbol{u}$ and $\boldsymbol{v}$. By appropriate integration of $\Omega(u,v,\omega)$, we have created a family of intracules that provide information about various combinations of u, v, and ω.[10,12]

Parts II and III of this series[13,14] have focused on the dot intracule $D(x)$, the quasidensity of finding two electrons with $\boldsymbol{u}\cdot\boldsymbol{v}=x$. This intracule offers a natural and efficient starting point for correlation energy calculations because it contains information about interelectronic positions and momenta and because its Fourier transform is available in closed form.[14] Our electron correlation model is based on the primary conjecture that the correlation energy is a universal functional of $\Omega(u,v,\omega)$ and the secondary conjectures,

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u,v,\omega)G(u,v,\omega)d\omega dv du, \tag{1}$$

$$E_c = \int_{-\infty}^\infty D(x)G(x)dx, \tag{2}$$

where $G(u,v,\omega)$ and $G(x)$ are universal kernels.

Until now, our assessment of such intracule-based correlation models has been based entirely on intracules generated from HF wave functions expanded in the 6–311G basis set and we have assumed, perhaps optimistically, that this basis is sufficiently large that it has not introduced any artifacts into our results. In the present work, we address this issue directly by investigating the basis set dependence of $P(u)$ and $D(x)$ and exploring the extent to which basis set effects on $D(x)$ affect the correlation energies obtained from the dot ansatz (2). All calculations were performed using a locally modified version of the Q-CHEM quantum chemistry package[15] and we use atomic units throughout.

II. BASIS SET EFFECTS ON INTRACULES

If the wave function is expanded in a one-electron basis set $\{\chi_\mu\}$, an intracule I can be expressed as

$$I = \sum_{\mu\nu\lambda\sigma} \Gamma_{\mu\nu\lambda\sigma}[\mu\nu\lambda\sigma]_I, \tag{3}$$

where $\Gamma_{\mu\nu\lambda\sigma}$ is the two-particle density matrix[16] and $[\mu\nu\lambda\sigma]_I$ are the associated intracule integrals. In the case of Gaussian basis functions, the position integrals $[ssss]_P$ and dot integrals $[ssss]_D$ are straightforward[12,13] and integrals of higher angular momentum can be found by differentiation with re-

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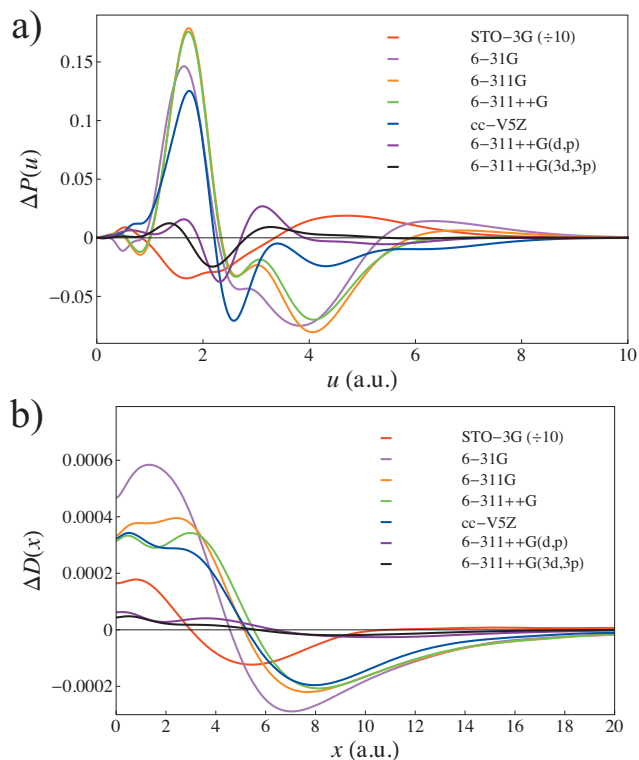[b)]Electronic mail: peter.gill@anu.edu.au.

FIG. 1. (Color) Difference intracules for CH_4 with respect to the HF/$6\text{-}311\text{+}\text{+}G(3df,3pd)$ reference in (a) position space and (b) dot space.

FIG. 2. (Color) Normalized average difference intracules for the G1 data set with respect to the HF/$6\text{-}311\text{+}\text{+}G(3df,3pd)$ reference in (a) position space and (b) dot space.

spect to the Cartesian centers of the basis functions, as first suggested by Boys.[17]

Position and dot intracules for the 18 atoms and 56 molecules of the G1 data set[18] have been calculated from HF wave functions with Pople basis sets of increasing complexity. With the exception of 6–31G, each member of the series 6–31G, 6–311G, 6-311++G, 6-311++G(d,p), 6-311++G$(3d,3p)$, and 6-311++G$(3df,3pd)$ is a superset of the previous basis with additional diffuse or polarization functions, thus allowing us unambiguously to ascribe intracule differences to those modifications. In addition, we explored the STO-3G basis set as a low-level marker and the nonpolarized part of Dunning's cc-pV5Z basis set (here denoted cc-V5Z)[19] as an indicator for how well the triple-split-valence 6–311G set spans sp space.

Taking the 6-311++G$(3df,3pd)$ intracules as a benchmark (I_{Ref}), we have used the difference intracule

$$\Delta I = I_{Ref} - I \qquad (4)$$

as a measure of basis set effect. To illustrate this, Fig. 1 shows several difference intracules for methane.

The trends in Figs. 1(a) and 1(b) are similar. As expected, STO-3G differences are much larger than the rest (note the scale of the STO-3G plots) and there is a marked decrease in error by going to 6–31G. A slight overall improvement is observed with the 6–311G basis yet the addition of diffuse functions does little to change the behavior of $\Delta P(u)$ or $\Delta D(x)$. We do, however, observe significant improvement upon inclusion of the polarization functions in the 6-311++G(d,p) basis. The addition of further polarization functions yields only a slight improvement.
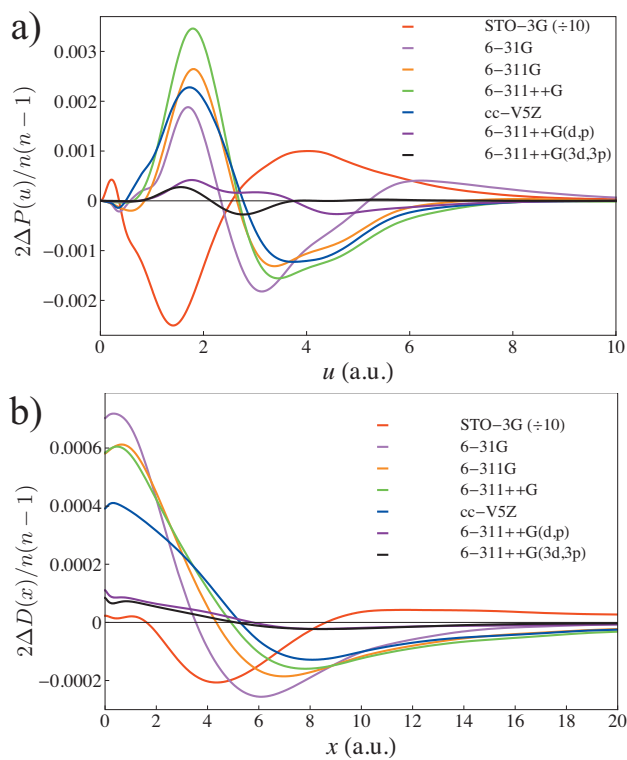
Because ΔI is proportional to the number of electron pairs (n_p), we have plotted the renormalized difference intracule ($\Delta I/np$), averaged over all atoms and molecules in the G1 data set. These data, presented in Fig. 2 allow us to examine consistent trends in the shape of ΔP and ΔD across the data set. The similarity between Figs. 1 and 2 reveals that the gross basis set effects on the intracules of methane are also present in many other molecules. The persistence of this structure in the averaged difference intracules demonstrates consistent trends in basis set effects across the G1 data set.

We see from Fig. 2(a) that, when one moves from STO-3G to the large reference basis set, there is a reduction in the probability of finding electrons close together ($u \approx 1.5$) and a corresponding increase in the likelihood of finding them further apart ($u \approx 4$). One can think of such a change as a "basis hole," not unlike the "correlation hole" first discussed by Coulson and Neilson.[1] Figure 2(b) reveals a comparable "basis hole" in the dot intracule.

An unexpected phenomenon arises, however, when we improve the quality of the sp basis without adding polarization functions. The curves for 6–31G, 6–311G, 6-311++G, and cc-V5Z in Fig. 2(a) show that such bases overcompensate for the shortcomings of STO-3G and predict that electrons tend to be further apart than they are in the large reference basis. The resulting "basis antiholes" imply that the electrons move closer together when polarization functions are included and, although this is counterintuitive, it is confirmed by the observation that the electron repulsion energy E_J usually follows the trend

TABLE I. $100\Delta_P$ and $100\Delta_D$ from various basis sets for the molecules in the G1 data set. The superscript indicates the basis set of the difference intracule from which Δ_P or Δ_D was calculated. (1) STO-3G, (2) 6-31G, (3) 6-311G, (4) 6-311++G, (5) cc-V5Z, (6) 6-311++G(d,p), and (7) 6-311++G($3d,3p$).

Molecule	Δ_P^1	Δ_P^2	Δ_P^3	Δ_P^4	Δ_P^5	Δ_P^6	Δ_P^7	Δ_D^1	Δ_D^2	Δ_D^3	Δ_D^4	Δ_D^5	Δ_D^6	Δ_D^7
H	0	0	0	0	0	0	0	0	0	0	0	0	0	0
He	7.24	0.54	0	0	0.23	0	0	4.02	0.78	0	0	0.36	0	0
Li	22.59	2.75	0.02	0	0.87	0	0	19.83	2.79	0.01	0	0.22	0	0
Be	22.15	4.62	0.47	0	0.40	0	0	14.74	3.33	0.41	0	0.02	0	0
B	25.00	4.43	0.69	0.12	0.63	0.18	0	13.98	2.20	0.30	0.41	0.31	0.10	0
C	16.27	2.68	0.63	0.07	0.66	0.07	0	7.37	1.36	0.25	0.17	0.17	0.06	0
N	10.67	0.76	0.60	0	0.69	0	0	5.44	0.41	0.25	0	0.22	0	0
O	12.59	1.04	0.86	0.05	0.75	0.02	0.03	5.39	0.36	0.36	0.10	0.23	0.03	0.03
F	13.51	1.62	0.90	0.03	0.83	0.01	0.02	5.49	0.56	0.35	0.07	0.25	0.01	0.02
Ne	14.89	1.75	0.94	0	0.90	0	0	5.83	0.58	0.35	0	0.26	0	0
Na	21.44	0.65	0.04	0	0.43	0	0	16.99	0.24	0.02	0	0.22	0	0
Mg	23.15	0.33	0.07	0	0.20	0	0	17.83	0.10	0.04	0	0.08	0	0
Al	21.53	0.22	0.09	0.15	0.12	0.10	0	16.27	0.11	0.12	0.17	0.19	0.06	0
Si	16.27	0.25	0.08	0.07	0.12	0.06	0	11.50	0.07	0.04	0.10	0.09	0.03	0
P	13.65	0.62	0.50	0	0.54	0	0	8.96	0.19	0.26	0	0.12	0	0
S	11.65	0.43	0.38	0.06	0.30	0.03	0.04	7.15	0.12	0.26	0.10	0.07	0.04	0.04
Cl	7.36	0.51	0.35	0.04	0.42	0.02	0.03	3.98	0.15	0.23	0.07	0.09	0.03	0.03
Ar	7.57	0.29	0.11	0	0.14	0	0	4.25	0.12	0.09	0	0.03	0	0
H_2	4.66	2.50	1.86	1.86	1.70	0.21	0.02	4.40	2.67	1.99	1.95	1.81	0.13	0.02
LiH	7.61	3.82	1.48	1.43	0.95	0.49	0.08	3.42	2.52	0.84	0.83	0.58	0.28	0.05
BeH	11.52	2.28	1.14	0.93	2.52	0.16	0.10	5.19	0.92	0.51	0.49	8.32	0.07	0.05
Li_2	9.89	1.79	0.42	0.36	0.36	0.04	0.05	6.70	1.09	0.18	0.15	0.19	0.10	0.09
CH	9.19	1.31	0.88	0.86	0.65	0.11	0.04	4.34	1.04	0.56	0.57	0.43	0.06	0.02
NH	6.86	0.74	0.80	0.90	0.53	0.11	0.01	5.04	0.83	0.66	0.53	0.39	0.09	0.01
$CH_2(^1A_1)$	5.60	1.03	1.22	1.28	1.06	0.18	0.05	4.00	1.18	1.01	0.90	0.81	0.08	0.03
$CH_2(^3B_1)$	6.20	1.01	0.69	0.63	0.60	0.13	0.09	3.83	0.74	0.51	0.47	0.39	0.08	0.06
OH	8.31	0.97	0.85	0.85	0.44	0.10	0.04	5.85	0.87	0.63	0.47	0.30	0.06	0.04
NH_2	4.92	1.08	1.09	1.25	0.85	0.13	0.01	4.62	1.19	1.03	0.80	0.69	0.08	0.02
CH_3	3.87	0.73	0.66	0.60	0.49	0.14	0.10	2.84	0.61	0.54	0.55	0.46	0.11	0.07
HF	9.19	1.65	0.91	0.71	0.41	0.16	0.08	6.63	1.16	0.69	0.43	0.27	0.07	0.06
H_2O	6.02	1.24	1.06	1.11	0.59	0.13	0.06	5.86	1.37	1.02	0.72	0.59	0.07	0.07
NH_3	4.08	1.20	1.08	1.04	0.70	0.12	0.02	3.86	1.22	0.97	0.80	0.71	0.07	0.04
CH_4	2.27	0.66	0.66	0.59	0.44	0.13	0.08	2.03	0.77	0.64	0.59	0.51	0.09	0.05
LiF	8.95	1.55	0.92	0.47	0.74	0.26	0.03	6.68	0.66	0.43	0.28	0.17	0.16	0.03
CN	4.46	1.68	1.61	1.68	1.47	0.19	0.14	3.43	1.82	1.76	1.73	1.64	0.25	0.20
N_2	3.57	2.23	1.95	2.07	1.79	0.24	0.16	2.72	1.75	1.63	1.64	1.51	0.18	0.17
CO	3.99	2.18	1.96	1.95	1.61	0.22	0.16	3.03	1.68	1.58	1.52	1.32	0.28	0.22
HCN	3.46	1.33	1.34	1.43	1.28	0.21	0.14	2.62	1.47	1.42	1.36	1.26	0.22	0.20
C_2H_2	4.23	1.19	0.85	0.82	0.81	0.22	0.19	2.09	1.08	1.02	1.01	0.94	0.21	0.20
NO	3.71	2.08	1.80	1.87	1.43	0.29	0.14	3.67	1.79	1.66	1.68	1.30	0.23	0.22
HCO	3.47	1.35	1.33	1.37	1.08	0.16	0.14	3.58	1.40	1.32	1.19	1.04	0.19	0.20
$SiH_2(^1A_1)$	6.99	1.50	1.53	1.53	1.41	0.17	0.09	4.14	1.16	1.03	1.07	1.02	0.08	0.02
$SiH_2(^3B_1)$	8.42	1.12	1.13	1.06	1.96	0.10	0.09	5.07	0.81	0.71	0.72	0.96	0.06	0.03
O_2	4.32	1.86	1.52	1.68	1.15	0.43	0.15	3.52	1.51	1.28	1.40	1.22	0.25	0.26
H_2CO	2.34	1.03	1.04	1.12	0.85	0.15	0.12	3.22	1.41	1.32	1.16	1.02	0.24	0.26
C_2H_4	2.47	0.58	0.55	0.61	0.56	0.14	0.10	1.74	0.66	0.65	0.65	0.59	0.21	0.19
PH_2	6.14	1.35	1.39	1.38	1.28	0.19	0.10	4.15	1.01	1.02	0.98	0.90	0.10	0.04
SiH_3	5.84	1.41	1.51	1.49	1.29	0.13	0.12	3.26	1.16	1.04	1.06	1.00	0.11	0.04
HCl	5.84	0.69	0.73	0.65	0.67	0.08	0.07	4.02	0.42	0.51	0.46	0.39	0.06	0.03
H_2S	5.65	1.24	1.25	1.24	1.09	0.15	0.12	4.30	0.88	0.95	0.91	0.80	0.11	0.05
PH_3	4.29	1.63	1.67	1.65	1.52	0.23	0.13	3.98	1.31	1.29	1.26	1.18	0.14	0.04
SiH_4	4.02	1.68	1.86	1.81	1.58	0.17	0.14	3.10	1.48	1.36	1.36	1.29	0.12	0.05
F_2	5.65	0.64	0.85	0.91	0.60	0.42	0.19	4.08	0.91	0.86	0.89	0.61	0.46	0.33
H_2O_2	3.26	1.04	0.93	1.06	0.69	0.32	0.12	4.26	1.39	1.20	1.12	0.89	0.34	0.21
N_2H_4	2.12	0.93	0.78	0.74	0.57	0.15	0.05	2.91	1.29	1.05	0.94	0.80	0.23	0.15
H_3COH	1.83	0.67	0.67	0.69	0.53	0.13	0.07	3.17	1.13	0.98	0.79	0.68	0.21	0.20
C_2H_6	1.39	0.61	0.63	0.61	0.58	0.11	0.05	1.43	0.59	0.45	0.42	0.33	0.12	0.10
CO_2	3.42	2.12	2.01	2.05	1.92	0.28	0.23	2.60	1.60	1.57	1.54	1.40	0.31	0.44
CS	4.40	1.66	1.53	1.57	1.46	0.23	0.16	3.38	1.44	1.34	1.36	1.26	0.24	0.18

TABLE I. (*Continued.*)

Molecule	Δ_P^1	Δ_P^2	Δ_P^3	Δ_P^4	Δ_P^5	Δ_P^6	Δ_P^7	Δ_D^1	Δ_D^2	Δ_D^3	Δ_D^4	Δ_D^5	Δ_D^6	Δ_D^7
Na_2	9.54	0.44	0.18	0.14	0.23	0.11	0.02	9.01	0.31	0.07	0.08	0.14	0.03	0.01
SiO	4.68	1.87	1.81	2.01	1.80	0.36	0.17	3.56	1.70	1.43	1.45	1.33	0.23	0.11
SO	4.34	1.57	1.53	1.63	1.43	0.36	0.24	3.72	1.35	1.29	1.26	1.12	0.23	0.19
ClO	2.93	1.25	1.22	1.17	0.99	0.35	0.23	3.58	0.98	0.99	0.96	0.84	0.26	0.20
ClF	2.84	0.89	0.93	0.91	0.80	0.36	0.19	3.61	0.75	0.78	0.75	0.64	0.31	0.27
HOCl	2.71	0.86	0.90	0.86	0.70	0.31	0.17	3.39	0.84	0.84	0.79	0.68	0.26	0.16
CH_3Cl	2.75	0.69	0.69	0.62	0.56	0.12	0.07	2.63	0.72	0.65	0.63	0.54	0.21	0.16
CH_3SH	2.75	0.84	0.88	0.85	0.71	0.12	0.08	2.82	0.83	0.80	0.77	0.67	0.20	0.15
NaCl	4.47	0.44	0.65	0.52	0.44	0.13	0.08	2.85	0.19	0.45	0.36	0.25	0.08	0.04
Si_2	7.42	2.84	1.95	1.61	2.77	0.73	0.12	3.13	0.77	0.51	1.03	0.75	0.29	0.05
P_2	5.46	2.01	2.20	2.09	1.92	0.64	0.23	2.81	1.46	1.50	1.47	1.36	0.37	0.18
S_2	4.69	1.85	1.68	1.60	1.53	0.51	0.29	2.87	1.25	1.20	1.17	1.09	0.33	0.24
SO_2	2.95	2.16	2.19	2.25	1.95	0.51	0.26	3.47	2.04	1.91	1.91	1.73	0.39	0.34
Cl_2	2.89	1.25	1.28	1.09	0.85	0.40	0.29	3.04	0.85	0.81	0.77	0.70	0.26	0.17
Si_2H_6	2.30	1.63	1.68	1.66	1.50	0.11	0.07	2.95	0.79	0.77	0.76	0.72	0.19	0.15
Mean absolute errors														
Atoms only	14.86	1.31	0.37	0.03	0.46	0.03	0.01	9.39	0.75	0.18	0.07	0.16	0.02	0.01
Molecules only	4.95	1.39	1.21	1.19	1.08	0.23	0.12	3.80	1.16	0.99	0.95	0.98	0.18	0.13
Atoms and molecules	7.36	1.37	1.01	0.91	0.93	0.18	0.09	5.18	1.06	0.79	0.73	0.78	0.14	0.10

$$E_J[\text{STO-3G}] > E_J[6\text{-}311++\text{G}(3df,3pd)]$$
$$> E_J[6\text{-}31\text{G}].$$

The trend in E_J for a given basis (i.e., $E_J[6\text{-}311++\text{G}(3df,3pd)] - E_J[\text{Basis}] = \Delta E_J$) is also exactly determined from the difference intracules by the relation

$$\Delta E_J + \Delta E_K = \int_0^\infty \Delta P(u)u^{-1}du, \qquad (5)$$

which emphasizes the importance of the short-range part of the intracule in determining the repulsion energy. Thus, a basis hole is indicative of a *positive* deviation in E_J from the reference and a basis antihole is indicative of a *negative* deviation.

Of course, this effect is more than counterbalanced by the nuclear attraction energy and the *total* energy of the $6\text{-}311++\text{G}(3df,3pd)$ wave function is lower than that of the $6\text{-}31\text{G}$ wave function, despite the electrons in the former tending to be closer together. Such an effect is reminiscent of the secondary Coulomb hole recently observed[4] in the helium atom, wherein correlation is found to *reduce* $P(u)$ for large u.

The polarization functions in $6\text{-}311++\text{G}(d,p)$ largely eliminate the basis antihole and yield position and dot intracules that are probably very close to the HF limit.

It is convenient to be able to reduce ΔI to a single number that measures the overall faithfulness of the intracule to its benchmark. Because our intracules are always normalized to the number $n(n-1)/2$ of pairs of electrons, the integral of ΔI vanishes identically. However, the integral of $|\Delta I|$ is nonnegative and the renormalized quantities,

$$\Delta_P = \frac{2}{n(n-1)} \int_0^\infty |\Delta P(u)|du, \qquad (6)$$

$$\Delta_D = \frac{2}{n(n-1)} \int_{-\infty}^\infty |\Delta D(x)|dx, \qquad (7)$$

provide useful measures of the deviation of an intracule from its benchmark. We have also explored the use of the maximum difference between intracules to quantify basis set effects but have found that the trends in this quantity are very similar to those for Δ_P and Δ_D. The Δ_P and Δ_D values for each basis set and each atom or molecule in the G1 data set are listed in Table I.

The results in Table I reinforce the qualitative conclusions drawn from Figs. 1 and 2. The greatest improvement in the quality of the intracule is achieved in going from STO-3G (which is particularly poor for atoms) to 6–31G. After this, the next most significant improvement comes from the addition of the first set of polarization functions to the triple-split-valence 6–311G and only a very slight improvement is obtained from the higher polarization functions. Again, diffuse functions do not appear to have any significant effect on the quality of the intracule, although it should be noted that there are no anionic systems in the G1 data set.

The cc-V5Z basis (which includes only s and p functions for heavy atoms and s functions for H and He) appears similar to 6–31G, 6–311G, and 6-311++G, indicating that the effect of additional valence functions beyond those in 6-311++G is modest.

III. BASIS SET EFFECTS ON CORRELATION ENERGIES

A correlation model based on the dot intracule ansatz (2) requires a kernel and we have explored[13,14]

TABLE II. The exact correlation energy E_c^{exact} and errors ΔE_c^{Basis} from various basis sets for the molecules in the G1 data set. All values in mE_h. (1) STO-3G, (2) 6-31G, (3) 6-311G, (4) 6-311++G, (5) cc-V5Z, (6) 6-311++G(d,p), (7) 6-311++G$(3d,3p)$, and (8) 6-311++G$(3df,3pd)$.

Molecule	$-E_c^{exact}$	ΔE_c^1	ΔE_c^2	ΔE_c^3	ΔE_c^4	ΔE_c^5	ΔE_c^6	ΔE_c^7	ΔE_c^8
H	0	0	0	0	0	0	0	0	0
He	42	0	1	1	1	1	1	1	1
Li	45	1	0	0	0	1	0	0	0
Be	94	−12	−13	−12	−12	−12	−12	−12	−12
B	121	−11	−10	−8	−8	−8	−9	−9	−9
C	151	−5	−1	0	1	0	0	0	0
N	185	5	13	14	14	14	14	14	14
O	249	−3	5	5	5	4	4	4	4
F	318	−8	−1	−1	−1	−1	−1	−1	−1
Ne	391	−9	−2	−2	−2	−2	−2	−2	−2
Na	396	−1	−6	−8	−8	−7	−8	−8	−8
Mg	438	−17	−14	−14	−14	−14	−14	−14	−14
Al	465	−16	−11	−11	−11	−11	−12	−12	−12
Si	500	−17	−9	−9	−9	−9	−10	−10	−10
P	540	−17	−5	−1	−3	−4	−3	−3	−3
S	597	−14	0	1	0	0	−1	−1	−1
Cl	658	−11	7	9	8	7	7	7	7
Ar	723	−3	18	18	18	18	18	18	18
H_2	41	−2	−1	−1	−1	−1	−1	−1	−1
LiH	83	6	6	7	7	7	7	7	7
BeH	93	5	5	5	6	14	6	6	6
Li_2	124	4	4	4	5	5	5	5	5
CH	194	−7	−4	−3	−3	−3	−3	−3	−3
NH	236	5	13	13	14	14	14	14	14
$CH_2(^1A_1)$	239	−7	−4	−4	−4	−4	−4	−4	−4
$CH_2(^3B_1)$	208	23	30	31	32	31	32	32	32
OH	309	−5	3	4	4	4	5	5	5
NH_2	287	13	20	20	21	20	21	21	21
CH_3	254	38	45	45	46	45	45	45	45
HF	389	−16	−5	−4	−4	−4	−3	−3	−3
H_2O	371	−2	8	9	10	9	11	11	11
NH_3	340	26	31	32	33	32	33	33	33
CH_4	299	55	60	60	60	60	59	59	59
LiF	441	−23	−4	−3	−2	−2	−2	−2	−2
CN	483	−66	−63	−63	−63	−63	−58	−58	−58
N_2	549	−61	−59	−58	−58	−59	−57	−57	−57
CO	535	−48	−46	−45	−45	−45	−45	−45	−44
HCN	515	−26	−23	−23	−23	−23	−22	−22	−22
C_2H_4	480	11	14	14	14	14	14	14	14
NO	596	−69	−63	−63	−64	−62	−61	−61	−61
HCO	553	−34	−26	−26	−26	−26	−25	−25	−25
$SiH_2(^1A_1)$	567	−2	7	7	7	7	7	6	6
$SiH_2(^3B_1)$	540	18	28	28	28	28	27	26	25
O_2	636	−59	−54	−54	−55	−56	−54	−54	−54
H_2CO	586	−17	−12	−12	−12	−12	−12	−12	−12
C_2H_4	518	49	54	54	53	52	53	52	53
PH_2	611	14	30	30	29	29	29	29	29
SiH_3	575	34	45	45	45	45	40	39	38
HCl	707	4	24	24	24	23	25	25	25
H_2S	683	14	33	31	32	32	33	33	33
PH_3	652	27	43	42	42	42	41	41	41
SiH_4	606	53	63	62	62	63	55	53	53
F_2	757	−83	−75	−74	−76	−77	−74	−74	−73
H_2O_2	711	−43	−31	−30	−32	−33	−30	−30	−30
N_2H_4	641	25	33	34	32	31	33	33	33
H_3COH	629	29	38	38	37	36	37	37	37
C_2H_6	561	91	96	96	95	94	94	94	94
CO_2	876	−59	−53	−52	−51	−52	−49	−50	−50
CS	867	−47	−34	−33	−33	−33	−31	−31	−30

TABLE II.   (*Continued.*)

Molecule	$-E_c^{exact}$	ΔE_c^1	ΔE_c^2	ΔE_c^3	ΔE_c^4	ΔE_c^5	ΔE_c^6	ΔE_c^7	ΔE_c^8
Na$_2$	819	−8	−6	−9	−8	−6	−8	−8	−8
SiO	879	−61	−49	−48	−46	−46	−46	−45	−45
SO	957	−48	−34	−33	−34	−35	−31	−32	−32
ClO	1002	−46	−28	−28	−29	−30	−27	−26	−26
ClF	1063	−52	−34	−34	−36	−36	−33	−33	−33
HOCl	1045	−32	−14	−13	−14	−15	−11	−11	−11
CH$_3$Cl	968	42	59	58	58	57	58	58	58
CH$_3$SH	946	53	69	68	68	67	68	68	68
NaCl	1101	12	30	31	30	31	31	31	31
Si$_2$	1077	−53	−19	−29	−39	−20	−39	−38	−38
P$_2$	1205	−45	−24	−21	−22	−24	−18	−17	−17
S$_2$	1275	−19	4	2	3	2	6	7	7
SO$_2$	1334	−96	−78	−76	−76	−78	−73	−74	−74
Cl$_2$	1380	−17	11	9	10	8	14	15	15
Si$_2$H$_6$	1183	97	117	113	113	114	100	98	97
Mean absolute errors									
Atoms only		8	6	6	6	6	6	6	6
Molecules only		34	33	33	34	33	32	32	32
Atoms and molecules		28	27	26	27	26	26	26	26

$$G(x) = c_D \cos k_0 x, \tag{8}$$

where $c_D = -76.95$ mE_h and $k_0 = 0.8474$ are parameters that have been optimized by fitting to the correlation energies of the first 18 atoms in the Periodic Table.

Table II lists the exact correlation energies[20] for each system in the G1 data set as well as errors,

$$\Delta E_c^n = E_c^{exact} - E_c^n, \tag{9}$$

in the correlation energies predicted from Eqs. (2) and (8), where the index n denotes which basis set has been used, in order of increasing polarization and size.

Examination of Table II reveals that errors in the correlation energies calculated from Eqs. (2) and (8) are remarkably insensitive to the basis set used. The mean absolute error (MAE) for the full test set changes by only 2 mE_h between the minimal STO-3G basis and the large 6-311+ +G(3df, 3pd) basis. We are relieved to find that our historical use of the triple-split-valence 6–311G basis appears to be justified.

The results in Table II were generated using parameters that were optimized using the 6–311G basis set. Alternatively, one may reoptimize c_D and k_0 for each basis set by

TABLE III. Reoptimized parameters for each basis and MAE for the first 18 atoms of the periodic table. c_D and MAE are given in mE_h.

Basis set	c_D	k_0	MAE
(1) STO-3G	−76.6	0.8405	5.1
(2) 6–31G	−77.0	0.8473	6.4
(3) 6–311G	−77.0	0.8474	6.4
(4) 6-311++G	−77.0	0.8475	6.4
(5) cc-V5Z	−77.1	0.8475	6.3
(6) 6-311++G(d,p)	−77.1	0.8475	6.4
(7) 6-311++G(3d,3p)	−77.1	0.8475	6.4
(8) 6-311++G(3df,3pd)	−77.1	0.8475	6.7

rms fitting the correlation energies of the first 18 atoms, as was done previously for the 6–311G basis.[13] This yields the lowest possible rms error for a given basis.

Table III lists the reoptimized parameters c_D and k_0 for each basis as well as MAE in the E_c calculated for the first 18 atoms of the periodic table. These results show that c_D and k_0 are also insensitive to the choice of basis. The MAE data also demonstrate that the correlation energies calculated with parameters optimized for the particular basis will not significantly improve the accuracy of the calculation.

IV. CONCLUDING REMARKS

We have calculated position and dot intracules for the first 18 atoms of the periodic table and all 56 molecules of the G1 data set using a series of Pople basis sets and the nonpolarized part of Dunning's cc-pV5Z basis to determine the effect of basis set on intracule shape and the sensitivity of correlation energies based on intracule functional theory.

Using Δ_P and Δ_D as a measure, we have shown that the difference between the low-level STO-3G intracules and the reference 6-311++G(3df, 3pd) intracules is small but can be reduced further by using the triple-split-valence 6–311G basis. We have also shown that diffuse functions do not significantly change the intracules although we note that there are no anionic systems in our test set. In addition, we have observed that polarization functions improve the intracules only slightly.

The correlation energy is even less sensitive to the basis set than the intracules are. We have demonstrated that E_c calculated using the dot ansatz is highly robust and we observe a 2 mE_h difference between the STO-3G and 6-311 ++G(3df, 3pd) mean absolute deviations across the entire test set of atoms and molecules.

Such observations provide an *a posteriori* justification

for the use of HF/6–311G wave functions in intracule functional theory.

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