Topological analysis of electron-electron interactions in atoms and molecules.

II. The correlation cage

Jerzy Cioslowski(a) and Guanghua Liu
Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006

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The concept of the correlation cage provides new insights into electron–electron interactions in atoms and molecules. The cage constitutes the domain in the space of interelectron distance vectors $\mathbf{R}$ within which correlation effects are substantial. Its shape and size are entirely determined by the topological properties of the electron intracule density $I(\mathbf{R})$, thus avoiding any references to ill-defined “uncorrelated” quantities. Integration of observables related to $I(\mathbf{R})$ over the correlation cage affords quantitative measures of electron correlation. The number of strongly correlated electron pairs $M_{\text{corr}}[I]$, their electron–electron repulsion energy $W_{\text{corr}}[I]$, and the cage volume $V_{\text{corr}}[I]$ that characterizes the spatial extent of electron correlation are functionals of $I(\mathbf{R})$. The ratio $k[I]$ of $I(0)V_{\text{corr}}[I]$ and $M_{\text{corr}}[I]$, which measures the strength of short-range correlation effects, is small for systems such as H$^+$ and closer to one for those with weaker correlation effects.

I. INTRODUCTION

Thorough understanding of electron correlation in Coulombic systems calls for rigorous analysis of observables derived from the two-particle density $\rho(\mathbf{r}_1, \mathbf{r}_2)$. Although even single numbers, such as the statistical coefficients first introduced by Kutzelnigg et al., provide valuable insights into electron correlation in atoms and molecules, a much more detailed picture of electron–electron interactions is afforded by the intracule density $I(\mathbf{R})$.

$$I(\mathbf{R}) = \int \rho(\mathbf{r} - \mathbf{R}/2, \mathbf{r} + \mathbf{R}/2) d\mathbf{r}.$$  (1)

The conventional approach to extracting quantitative data on electron correlation from $I(\mathbf{R})$ is based upon the concept of the Coulomb hole,,

$$\Delta I(\mathbf{R}) = I(\mathbf{R}) - I_{\text{HF}}(\mathbf{R}),$$  (2)

where $I_{\text{HF}}(\mathbf{R})$ is the “uncorrelated” intracule density obtained from the Hartree–Fock wave function. Since $\Delta I(\mathbf{R})$ is normalized to zero and assumes negative values at short interelectron distances $R=|\mathbf{R}|$, the surface at which $\Delta I(\mathbf{R})$ vanishes may be regarded as a natural boundary between the domains of strong and weak electron correlation. In spherically symmetrical atoms and also in other Coulombic systems provided spherical averaging of intracule densities is carried out first), such considerations lead to the definitions of the radius and volume of the Coulomb hole. Numerous studies employing this methodology have been reported in recent literature.

The disadvantage of the Coulomb hole formalism stems from its reliance on the Hartree–Fock wave function as the “uncorrelated” reference. Since the use of such a reference is obviously questionable for systems with significant non-dynamical electron correlation (such as molecules at the dissociation limit), analysis of electron–electron interactions based solely on the properties of $I(\mathbf{R})$ is clearly preferable.

The exact $I(\mathbf{R})$ possesses a cusp at $\mathbf{R}=0$. Although the reproduction of this cusp in approximate calculations requires either the inclusion of terms linear in $R$ in the electronic wave function or the use of the generalized Hiller–Sucher–Feinberg formalism, even low-level methods such as MP2 are capable of producing electron intracule densities with minima at the origin. On the other hand, the “uncorrelated” $I_{\text{HF}}(\mathbf{R})$ exhibits a maximum at $\mathbf{R}=0$. Consequently, topological analysis can be readily employed in the quantification of electron correlation effects, which manifest themselves with the presence of the electron–electron coalescence cusp (or a minimum) in $I(\mathbf{R})$.

Topological analysis of multivariate functions that describe physical observables has been widely used in quantum chemistry. When applied to the potential energy as a function of nuclear positions, it permits the partitioning of the potential energy hypersurface into catchment regions, each of them defining (within the Born–Oppenheimer approximation) a locally stable molecular geometry. Even more important, it gives rise to quantum-mechanical definitions of atoms and bonds in molecules that are based on topological properties of the one-electron density $\rho(\mathbf{r})$. Although topologies of many other quantities, such as the nuclear potential, the virial field, and the electron density Laplacian, have also been investigated, this type of analysis has been employed in conjunction with the electron intracule and extracule densities only very recently.

In this paper, the concept of the correlation cage is introduced in order to establish the connection between topological properties of the electron intracule density and quantitative aspects of electron correlation in atoms and molecules. The correlation cage constitutes the domain in the space of interelectron distance vectors $\mathbf{R}$ within which correlation effects are substantial. Its shape and size are entirely determined by the topological properties of the electron intracule density $I(\mathbf{R})$, thus avoiding any references to ill-defined “uncorrelated” quantities. Integration of observables related to $I(\mathbf{R})$ over the correlation cage affords quantitative measures of electron correlation. The number of strongly correlated electron pairs $M_{\text{corr}}[I]$, their electron–electron repulsion energy $W_{\text{corr}}[I]$, and the cage volume $V_{\text{corr}}[I]$ that characterizes the spatial extent of electron correlation are functionals of $I(\mathbf{R})$. The ratio $k[I]$ of $I(0)V_{\text{corr}}[I]$ and $M_{\text{corr}}[I]$, which measures the strength of short-range correlation effects, is small for systems such as H$^+$ and closer to one for those with weaker correlation effects. © 1999 American Institute of Physics. [S0021-9606(99)31004-7]
molecules. Definitions of the number of strongly correlated electron pairs and their electron–electron repulsion energy are proposed. Illustrative examples involving the $\text{H}^+$, $\text{H}_2$, and $\text{H}_2^+$ two-electron systems are presented.

II. TOPOLOGICAL PROPERTIES OF THE ELECTRON INTRACULE DENSITY

A. Basic concepts

Even in the absence of electron correlation, the topology of $I(\mathbf{R})$ is considerably more complex than that of $\rho(\mathbf{r})$.\textsuperscript{12,16} For this reason, it is appropriate to briefly review certain basic concepts of topological analysis prior to embarking upon the actual investigation of properties of the electron intracule density.

Let $F(\mathbf{R})$ be a continuous function of a three-dimensional position vector $\mathbf{R}=(X,Y,Z)$, such that

$$\forall F(\mathbf{R})>0, \lim_{\mathbf{R} \to \infty} F(\mathbf{R})=0. \quad (3)$$

Critical points at which the gradient of $F(\mathbf{R})$ vanishes are classified according to the numbers of the positive and negative eigenvalues, $n_+$ and $n_-$, of the corresponding Hessian.\textsuperscript{15} The notation $(\omega,\sigma)$, where the rank $\omega$ and the signature $\sigma$ equal $n_++n_-$ and $n_+-n_-$, respectively, is commonly used. Stable critical points of rank three occur in four varieties called attractors $(\sigma=-3)$, and the bond $(\sigma=-1)$, ring $(\sigma=1)$, and cage points $(\sigma=3)$. For the sake of convenience, the terms attractor and cage point also encompass respective cusps, i.e., local maxima and minima at which the gradient of $F(\mathbf{R})$ is discontinuous. Degenerate critical points of lower ranks are not considered here as they are of no importance to the analysis of $I(\mathbf{R})$.

Gradient paths, i.e., lines of steepest descent in $F(\mathbf{R})$, always originate at critical points. The set of all the gradient paths that emanate from a given attractor is known as an attractor basin. Some of those paths, called attractor interaction lines, terminate at bond points. A zero-flux surface sheet is the collection of the all gradient paths that stem from a particular bond point. Although most of these paths have infinite extents, some terminate at bond, ring, or cage points. The set of all the gradient paths (which may originate at attractors, bond points, or other ring points) that terminate at a given ring point defines a ring surface, whereas the two gradient paths that emanate from that point form a ring line. The ring line either terminates at one or two cage points, or has an infinite extent. Finally, all the gradient paths that begin at attractors, bond points, or ring points and terminate at a particular cage point are collectively called a cage. Cages have ring surfaces as faces, attractor interaction lines as edges, and attractors as vertices. Ring surfaces are demarcated by attractor interaction lines, whereas the borders of attractor basins are delineated by zero-flux surfaces sheets, which coalesce only at ring lines and are pierced by attractor interaction lines at bond points. Ring surfaces come together only at attractor interaction lines and are crossed by ring lines at ring points.

Functions that exhibit cylindrical symmetry, i.e., those that depend only on $(X^2+Y^2)^{1/2}$ and $Z$, possess unique topological properties. In particular, all of their critical points lie on the $z$ axis. The only possible connectivities of these points are: attractor–bond point, attractor–cage point, bond point–ring point, and ring point–cage point. The presence of even one ring or cage point implies the existence of at least one critical circle, i.e., a closed curve of constant $(X^2+Y^2)^{1/2}$ at which $F(\mathbf{R})$ is constant and its gradient vanishes. There are three types of stable critical circles denoted in accordance with their signatures as $(2,-2)$, $(2,0)$, and $(2,2)$. Among the large number of possible arrangements of critical points and circles, the one involving two attractors, a cage point, and a $(2,0)$ circle is of relevance to the present study. The gradient paths that emanate from this critical circle delineate the zero-flux surface that separates two attractor basins, whereas the terminating paths define the cage face.

Topologies of functions with spherical symmetry, i.e., those depending only on $R=|\mathbf{R}|=(X^2+Y^2+Z^2)^{1/2}$, are much less involved. There is either an attractor or a cage point at $R=0$. In addition, surfaces of constant $R$ and $F(\mathbf{R})$ at which the gradient of $F(\mathbf{R})$ vanishes (critical spheres) may be present. Radial maxima, i.e., $(1,-1)$ critical spheres, constitute both cage faces and delocalized attractors, whereas $(1,1)$ critical spheres (which are radial minima) serve as both delocalized cage points and zero-flux surfaces that demarcate attractor basins.

B. The correlation cage

The connections between the topology of $\rho(\mathbf{r})$ and various elements of chemical structure are well known.\textsuperscript{15} The attractors usually coincide with nuclei, although non-nuclear attractors\textsuperscript{20} and one-electron densities that lack maxima at some nuclei\textsuperscript{15} are occasionally encountered. The attractor interaction lines indicate the presence of chemical bonds\textsuperscript{15} or strong steric repulsions.\textsuperscript{21} Pairs of attractors connected by more than one interaction line are quite rare.\textsuperscript{22} Thus far, neither critical circles nor spheres have been found among the topological features of ground-state one-electron densities of atoms and molecules.

“Uncorrelated” electron intracule densities calculated within the Hartree–Fock approximation are characterized by complicated topologies.\textsuperscript{12} In addition to attractors at $\mathbf{R}=0$, they possess local maxima that occur at internuclear distance vectors (note, however, that attractors attributable to nuclear pairs involving hydrogens are often missing). Thanks to the inherent symmetry of $I(\mathbf{R})$, the critical points and their connecting gradient paths exhibit centers of inversion. Unusual topological features, such as attractors linked by multiple interaction lines, are sometimes present.

This complexity is further increased by electron correlation. With the central attractor replaced by a cage point, the pattern of critical points and their connectivities is greatly altered at small interelectron distances. The most important of these changes is the appearance of a correlation cage, which arises from the presence of the electron–electron coalescence cusp in $I(\mathbf{R})$. Since this cusp stems directly from the reduction in the probability of finding one electron in the vicinity of another, the elucidation of properties of correlation cages is of great importance to quantitative analysis of electron correlation in Coulombic systems.
Several of these properties are worth mentioning. In addition to the center of inversion, correlation cages possess all the symmetry elements of the underlying electronic wave functions. They are size intensive, i.e., independent of the size of a system composed of noninteracting identical entities. Critical points located on the faces of correlation cages serve as anchors for gradient paths that connect them to outside attractors. Thus, in a sense, these cages act as “fat attractors” that replace the attractors at $R=0$ present in $I_{HF}(R)$.

Let $\Omega[I]$ stand for the correlation cage pertaining to a given $I(R)$. The average number of electron pairs within $\Omega[I]$ equals

$$M_{\text{corr}}[I] = \int_{\Omega[I]} I(R) d\mathbf{R}. \quad (4)$$

The contribution of these strongly correlated electron pairs to the electron–electron repulsion energy is given by

$$W_{\text{corr}}[I] = \int_{\Omega[I]} I(R)|\mathbf{R}^{-1}| d\mathbf{R}. \quad (5)$$

Both $M_{\text{corr}}[I]$ and $W_{\text{corr}}[I]$ are size extensive but not size consistent. On the other hand, the volume of the correlation cage,

$$V_{\text{corr}}[I] = \int_{\Omega[I]} d\mathbf{R}, \quad (6)$$

which characterizes the spatial extent of electron correlation, is size intensive. The unitless ratio,

$$\kappa[I] = I(0)V_{\text{corr}}[I]/M_{\text{corr}}[I], \quad 0 < \kappa[I] < 1, \quad (7)$$

measures the degree of variation in the electron intracule density within the correlation cage, i.e., the relative reduction in the magnitude of $I(R)$ at $\mathbf{R} \to 0$. Consequently, this ratio quantifies the strength of short-range correlation.

![FIG. 1. The correlation cage of the $H^+$ ion. The cage point and the (1,−1) critical sphere, which also constitutes the cage face, are denoted by a star and a solid line, respectively. Values of $I(R)$ at the critical entities are listed.](image1)

![FIG. 2. The correlation cage of the $H_2$ molecule (positioned along the z axis). The cage point, the two attractors, and the (2,0) critical circle are denoted by a star, dots, and a broken line, respectively. Values of $I(R)$ at the critical entities are listed. The cage face is marked with a solid line in (a) and by a broken line in (b).](image2)

### III. NUMERICAL EXAMPLES

Two-electron atoms, ions, and molecules are the simplest systems that exhibit electron correlation. As such, they are ideally suited for illustrating properties of correlation cages.

Correlated electron intracule densities of the $H^+$, $H_2$, and $H_3^+$ species were computed from the MP2 energy-derivative two-electron reduced density matrices. Efficient algorithms for the calculation of $I(R)$ and its derivatives on large grids of points, and for automatic location of critical points were used in conjunction with the GAUSSIAN 94 suite of programs. Gradient paths were determined using a fourth-order Runge–Kutta integrator with a step size of 0.01 a.u. Numerical integrations within correlation cages [Eqs.
involved 16-point Gauss–Legendre quadratures in each direction. In order to rule out the possibility of variation in the topologies of $I(R)$ with the accuracy of the underlying electronic wave functions, three different basis sets were employed in the present calculations. The spd contracted functions taken from the aug-cc-pV5Z and aug-cc-pV6Z basis sets were used for all the systems under study. The topological features and correlation cages obtained with the latter basis set are displayed in Figs. 1–3. In addition, $I(R)$ of $\text{H}_2$ and $\text{H}_2^-$ were computed with the uncontracted ($20s10p10d$) even-tempered basis set (with the exponents scaled down in the case of $\text{H}_2^-$).

The spherical correlation cage of $\text{H}_2^-$ (Fig. 1) has a radius of $\sim$1.1 [a.u.] (Table I) and contains on average $\sim$2.5 $\times 10^{-2}$ electron pairs, which contribute $\sim$3.3$\times$10$^{-2}$ [a.u.] to the electron–electron repulsion energy (Table II). The topological features of $I(R)$ are particularly simple in this case, consisting of the central cage point and a $(1,-1)$ critical sphere that delineates the cage face. The ratio $\kappa[I]$ is quite small, indicating strong short-range electron correlation. There is a good agreement among the properties of the correlation cage computed with the three basis sets.

The spindle-shaped correlation cage of the $\text{H}_2$ molecule at equilibrium geometry (Fig. 2) possesses cylindrical symmetry. Its face is spanned by gradient paths connecting the equatorial $(2,0)$ critical circle with two attractors located at the cage poles that lie along the internuclear vector $R_{\text{HH}}$. The half of the pole–pole distance amounts to $\sim$1.0 [a.u.], whereas the circle radius is $\sim$0.6 [a.u.] (Table I). Thus, a substantial narrowing of the correlation cage, which brings its volume down to only about one-quarter of that in $\text{H}_2^-$, is
observed in the direction perpendicular to \(R_{\text{HH}}\). There are on average \(\sim 3.0 \times 10^{-2}\) electron pairs within the cage, their electron–electron repulsion energy amounting to \(\sim 6.3 \times 10^{-2}\) [a.u.] (Table II). The ratio \(\kappa[I]\) is substantially higher than that in \(\text{H}^+\).

With its six attractors, six bond points, two ring points, and one cage point, the topology of the electron intracule density of the \(\text{H}_3^+\) ion is much richer than those of \(\text{H}^-\) and \(\text{H}_2\) (Fig. 3). The set of 12 attractor interaction lines forms an almost perfect circle with a radius of \(\sim 0.9\) [a.u.] (Table I). The gradient paths connecting two apical ring points (located \(\sim 0.6\) [a.u.] above and below the plane containing the attractor interaction lines) with the bond points and the attractors form two ring planes that delineate the cage surface. These planes deviate very little from cylindrical symmetry. The correlation cage, which has a “flying saucer” shape, is \(\sim 20\%\) larger in volume than that of \(\text{H}_2\) (Table II).

There are interesting similarities between the correlation cages of \(\text{H}_2\) and \(\text{H}_3^+\). In both cases, the cages are \(\sim 0.6\) [a.u.] wide in the directions perpendicular to all of the internuclear distances vectors. On the other hand, the widths in the other directions are close to 1.0 [a.u.] (which is also the approximate radius of the correlation cage of \(\text{H}^-\)). In addition, the cages of \(\text{H}_2\) and \(\text{H}_3^+\) have comparable values of \(\kappa[I]\).

### IV. CONCLUSIONS

The concept of the correlation cage provides new insights into electron–electron interactions in atoms and molecules. The cage constitutes the domain in the space of interelectron distance vectors \(R\) within which correlation effects are substantial. Its shape and size are entirely deter-

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**TABLE I. Locations \(R\) of the critical entities in \(\text{H}^-, \text{H}_2, \) and \(\text{H}_3^+, \) and the corresponding values of \(I(R).\)**

<table>
<thead>
<tr>
<th>System</th>
<th>Entity</th>
<th>Basis set</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
<th>(I(R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^-)</td>
<td>Critical sphere</td>
<td>20s10p10d/hr</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>1.080 34</td>
<td>5.141 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV5Zb</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>1.076 06</td>
<td>5.134 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV6Zb</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>1.081 48</td>
<td>5.170 \times 10^{-3}</td>
</tr>
<tr>
<td>(\text{H}_3^+)</td>
<td>Attractor</td>
<td>20s10p10d/hr</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>0.972 09</td>
<td>2.819 \times 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV5Zb</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>0.969 49</td>
<td>2.818 \times 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV6Zb</td>
<td>0.000 00</td>
<td>0.000 00</td>
<td>0.972 65</td>
<td>2.818 \times 10^{-2}</td>
</tr>
<tr>
<td>(\text{H}_3^+)</td>
<td>Critical circle</td>
<td>20s10p10d/hr</td>
<td>0.000 00</td>
<td>0.607 99</td>
<td>0.000 00</td>
<td>2.163 \times 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV5Zb</td>
<td>0.000 00</td>
<td>0.612 43</td>
<td>0.000 00</td>
<td>2.159 \times 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aug-cc-pV6Zb</td>
<td>0.000 00</td>
<td>0.608 60</td>
<td>0.000 00</td>
<td>2.163 \times 10^{-2}</td>
</tr>
</tbody>
</table>

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**TABLE II. Properties of the correlation cages of \(\text{H}^-\), \(\text{H}_2\), and \(\text{H}_3^+\).**

<table>
<thead>
<tr>
<th>System</th>
<th>Basis set</th>
<th>(I(0))</th>
<th>(M_{\text{core}}[I])</th>
<th>(W_{\text{core}}[I])</th>
<th>(V_{\text{core}}[I])</th>
<th>(\kappa[I])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^-)</td>
<td>20s10p10d/hr</td>
<td>2.486 \times 10^{-3}</td>
<td>2.529 \times 10^{-2}</td>
<td>3.344 \times 10^{-2}</td>
<td>5.282</td>
<td>0.519</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pV5Zb</td>
<td>2.705 \times 10^{-3}</td>
<td>2.495 \times 10^{-2}</td>
<td>3.317 \times 10^{-2}</td>
<td>5.219</td>
<td>0.566</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pV6Zb</td>
<td>2.634 \times 10^{-3}</td>
<td>2.554 \times 10^{-2}</td>
<td>3.377 \times 10^{-2}</td>
<td>5.298</td>
<td>0.546</td>
</tr>
<tr>
<td>(\text{H}_3^+)</td>
<td>20s10p10d/hr</td>
<td>1.770 \times 10^{-2}</td>
<td>3.066 \times 10^{-2}</td>
<td>6.408 \times 10^{-2}</td>
<td>1.342</td>
<td>0.775</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pV5Zb</td>
<td>1.873 \times 10^{-2}</td>
<td>2.997 \times 10^{-2}</td>
<td>6.348 \times 10^{-2}</td>
<td>1.316</td>
<td>0.822</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pV6Zb</td>
<td>1.821 \times 10^{-2}</td>
<td>2.932 \times 10^{-2}</td>
<td>6.238 \times 10^{-2}</td>
<td>1.290</td>
<td>0.801</td>
</tr>
<tr>
<td>(\text{H}_3^+)</td>
<td>aug-cc-pV5Zb</td>
<td>2.032 \times 10^{-2}</td>
<td>4.037 \times 10^{-2}</td>
<td>7.991 \times 10^{-2}</td>
<td>1.588</td>
<td>0.799</td>
</tr>
</tbody>
</table>

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*All quantities in [a.u.].

The \(spd\) primitives only.

See Table I for the molecular geometries.
mined by the topological properties of the electron intracule density $I(R)$, thus avoiding any references to ill-defined “uncorrelated” quantities.

Integration of observables related to $I(R)$ over the correlation cage affords quantitative measures of electron correlation. The number of strongly correlated electron pairs $M_{\text{corr}}[I]$, their electron–electron repulsion energy $W_{\text{corr}}[I]$, and the cage volume $V_{\text{corr}}[I]$ that characterizes the spatial extent of electron correlation are functionals of $I(R)$. The ratio $\kappa[I]$ of $I(0)V_{\text{corr}}[I]$ and $M_{\text{corr}}[I]$, which measures the strength of short-range correlation effects, is small for systems such as $\text{H}^-$ and closer to one for those with weaker correlation effects.

The evolution of correlation cages in the course of bond dissociations and other chemical reactions is of particular interest. Work in this direction is currently in progress.

ACKNOWLEDGMENT

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