Reporte de avances del proyecto "Desarrollos y aplicaciones de topología químico cuántica" con identificador SC16-1-IG-99

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Resumen

El presente reporte constituye una breve descripción de la explotación de los recursos de supercómputo ofrecidos por DGTIC/UNAM mediante el proyecto SC16-1-IG-99. Al respecto, se incluyó correlación dinámica, y se separó en sus contribuciones de Fermi y de Coulomb en la partición energética de átomos cuánticos interactuantes (IQA, por sus siglas en inglés) por medio de la teoría de cúmulos acoplados[1,2] y se estableció un esquema para dividir la energía resultante de un cálculo basado en teoría del funcional de la densidad con IQA.[3] El método de análisis de función de onda de IQA se utilizó para el estudio de interacciones no covalentes. Más específicamente, se investigaron estados de transición formados a partir de ureas bifuncionales en adiciones de Michael[4] así como efectos cooperativos y anticooperativos del enlace de hidrógeno (EH) en distintas estructuras del hexámero de agua[5] y sistemas unidos por EHs asistidos por resonancia[6,7]. Asimismo, se graduaron un maestro en ciencias y dos estudiantes de licenciatura con el apoyo ofrecido mediante el proyecto antes referido.

Breve descripción de avances

La inclusión de correlación electrónica dinámica[1], se llevó a cabo por medio de (i) la consideración del Lagrangiano de cúmulos acoplados[8] (CC, por sus siglas en inglés)

$$L(\mathbf{t}, \bar{\mathbf{t}}, \lambda) = \langle \mathrm{HF}|\widehat{H}(\lambda)\exp(\widehat{T})|\mathrm{HF}\rangle + \sum_{\nu} \bar{t}_{\nu}\langle \nu|\exp(-\widehat{T})\widehat{H}(\lambda)\exp(\widehat{T})|\mathrm{HF}\rangle \tag{1}$$

donde $|\mathrm{HF}\rangle$ es el estado de Hartree-Fock, λ es un parámetro del cual depende el Hamiltoniano electrónico $\widehat{H}(\lambda)$ y $\bar{\mathbf{t}}$ son multiplicadores de Lagrange. Finalmente, $\mathbf{t}$ y $\widehat{T}$ son las amplitudes y el operador cúmulo dentro de la teoría CC[8]. Por otro lado, la división de la correlación electrónica en sus partes de Fermi y Coulomb[2] se hizo mediante funciones de densidad de transición HF/CC dependientes del espín,

$$\rho_1^{\sigma\sigma,\,\mathrm{HF/CC}}(\mathbf{r}_1,\ \mathbf{r}_1') = \sum_{pq} D_{p\sigma q\sigma}^{\mathrm{HF/CC}} \varphi_p^\star(\mathbf{r}_1')\varphi_q(\mathbf{r}_1)$$
$$= \sum_{pq} \langle \mathrm{HF}|\widehat{a}_{p\sigma}^\dagger \widehat{a}_{q\sigma}|\mathrm{CC}\rangle \varphi_p^\star(\mathbf{r}_1')\varphi_q(\mathbf{r}_1), \tag{2}$$

$$\rho_2^{\sigma\tau,\,\mathrm{HF/CC}}(\mathbf{r}_1,\ \mathbf{r}_2) = \sum_{pqrs} d_{p\sigma q\sigma r\tau s\tau}^{\mathrm{HF/CC}} \varphi_p^\star(\mathbf{r}_1)\varphi_q(\mathbf{r}_1)\varphi_r^\star(\mathbf{r}_2)\varphi_s(\mathbf{r}_2)$$
$$= \sum_{pqrs} \langle \mathrm{HF}| \left(\widehat{a}_{p\sigma}^\dagger \widehat{a}_{q\sigma} \widehat{a}_{r\tau}^\dagger \widehat{a}_{s\tau} - \delta_{\sigma\tau}\delta_{qr}\widehat{a}_{p\sigma}^\dagger \widehat{a}_{s\sigma} \right) |\mathrm{CC}\rangle \varphi_p^\star(\mathbf{r}_1)\varphi_q(\mathbf{r}_1)\varphi_r^\star(\mathbf{r}_2)\varphi_s(\mathbf{r}_2, \tag{3}$$

donde σ y τ representan las proyecciones de espín α y β, $|\mathrm{CC}\rangle$ es el estado de cúmulos acoplados y $\{\varphi\}$ es el conjunto de orbitales mediante el cual se construye el espacio de Fock del sistema.

La partición IQA consistente con cálculos basados en la teoría del funcional de la densidad[3] (DFT, por sus siglas en inglés), se hizo mediante el uso de energías de intercambio y correlación (xc, por sus iniciales en inglés) definidas dentro del marco conceptual de IQA, para escalar los términos monoelectrónicos y bielectrónicos de la energía xc de Kohn-Sham.

Los métodos de análisis de función de onda se utilizaron para estudiar

efectos cooperativos y anticooperativos del EH en $(\mathbf{H_2O})_6$ Se utilizó la partición IQA para establecer una jerarquía de fortaleza de enlaces de hidrógeno en función del carácter simple o doble de los donadores y aceptores de EH en cúmulos de agua.[5]

enlaces de hidrógeno asistidos por resonancia Se estudiaron los efectos no aditivos del EH en malondialdehído[6] y formas condensadas de este sistema[7]. Esta última investigación fue la base de la tesis de maestría del M. en C. Eduardo Alejandro Romero Montalvo.

catalizadores bifuncionales en la adición de Michael En este trabajo[4] se hizo un análisis de enlaces de hidrógeno y contactos π-π en tioureas bifuncionales utilizadas en la adición de Michael.

Cálculos realizados

La investigación descrita en el punto anterior incluyó

1. Cálculos de estructura electrónica que consistieron principalmente en optimizaciones de geometría de
   - distintas estructuras del hexámero de agua,[5].
   - sistemas unidos por enlaces de hidrógeno asistidos por resonancia, en particular malondialdehído[6] y moléculas resultantes de la fusión de este sistema[7].
   - cúmulos moleculares y estados de transición relevantes en tioureas bifuncionales con grupos metilo y trifluorometilo para la comparación de su actividad catalítica en adiciones de Michael[4].

2. Obtención de funciones de densidad de primer orden, $\rho_1(\mathbf{r}_1, \mathbf{r}_1')$ y $\varrho_1(\mathbf{r}_1)$, para su análisis topológico de acuerdo con la teoría cuántica de átomos en moléculas (QTAIM, por sus siglas en inglés).

3. Cálculo de densidades de pares, $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)$, para llevar a cabo la partición de la energía electrónica IQA.

El primer punto se realizó con programas de química cuántica estándar que se detallan en la siguiente sección. Los últimos dos aspectos implicaron cálculos computacionales muy costosos debido a que requieren la integración de los campos escalares $\rho_1(\mathbf{r}_1, \mathbf{r}_1')$, $\varrho_1(\mathbf{r}_1)$ y $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)$ en regiones altamente irregulares que son los átomos definidos por la teoría QTAIM. Para la partición IQA en particular, consideramos esferas β con radios que fueron parcialmente optimizados. El valor inicial de tales radios fue del 90 % de la distancia de un núcleo a su punto crítico de enlace[9] más cercano. También se tomaron en cuenta mallas de integración muy finas para obtener una precisión numérica adecuada para los cálculos tipo IQA. Más específicamente, se utilizaron mallas angulares de Lebedev con armónicos esféricos con $l = 10$. Puesto que se emplearon esferas β en todos los casos, fue necesario seleccionar mallas radiales interiores y exteriores, que en las integraciones más complicadas requirieron 900 y 800 puntos. Finalmente, el trabajo de investigación de las referencias [1] y [2] requirió la obtención de funciones $\rho_1(\mathbf{r}_1, \mathbf{r}_1')$ y $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)$ mediante metodologías establecidas en el grupo. Tales densidades fueron probadas para confirmar si mediante ellas se recuperaba la energía electrónica de un sistema dado.

Software utilizado

Los cálculos de estructura electrónica en los cuales se basaron los trabajos descritos previamente fueron realizados en los programas Gaussian 09 y Gamess Us. La confirmación de que las funciones de densidad de primero y de segundo orden reportadas en las referencias [1] y [2] fueran consistentes con la energía electrónica de los sistemas examinados fue hecha con el programa Imolint[10] La entrada de este programa consiste en las matrices de uno y dos electrones, así como los orbitales subyacentes al espacio de Fock de un sistema. Esta información permite construir los campos escalares $\rho_1(\mathbf{r}_1, \mathbf{r}_1')$ y $\varrho_2(\mathbf{r}_1, \mathbf{r}_1')$ con lo cual Imolint calcula la energía electrónica del sistema. La partición electrónica IQA se llevo a cabo con el programa Promolden[11].

Una línea de investigación reciente que se ha tomado en el grupo de trabajo es el enriquecimiento de biogas por medio de redes metal orgánicas (MOF, por sus siglas en inglés) con los códigos Raspa y Lammps. Con estos programas se han estudiado las propiedades de adsorción, separación, y difusión de más de veinte MOFs en combinación con CO_2, CH_4 y sus mezclas. Actualmente, se utiliza Gaussian 09 y Q-chem para obtener información más detallada acerca de las interacciones entre los gases y los sitios de adsorción en las MOFs de interés.

Recursos utilizados

Se utilizaron 554386.85 horas-CPU de cómputo aprobadas en el proyecto.

Lista de colaboradores

- Estudiantes de la UNAM
  - Q. Marco Antonio Tlatelpa Iglesias.
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  - M. en C. Rodrigo Chávez Calvillo.
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  - M. en C. Eduardo Alejandro Romero Montalvo.
  - Dr. Eddy Ivanhoe Jiménez Gutiérrez.
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  - M. en C. José Manuel Guevara Vela.
  - Dr. Evelio Francisco Miguelez.
  - Dra. María Aurora Costales Castro.
  - Dr. Ángel Martín Pendás.
- Universidad de Guanajuato
  - Dr. Marco Antonio García Revilla.
- Universidad del País Vasco
  - Dr. Eduard José Matito Gras.

Lista de artículos publicados

1. F. J. Holguín-Gallego, R. Chávez-Calvillo, M. García-Revilla, E. Francisco, Á. Martín-Pendás, T. Rocha-Rinza "Electron correlation in the interacting quantum atoms partition via coupled cluster lagrangian densities" *J. Comput. Chem.* **37**, 1753 (2016).

2. J. M. Guevara-Vela, E. Romero-Montalvo, V. A. Mora-Gómez, R. Chávez-Calvillo, M. García-Revilla, E. Francisco, A. Martín Pendás, T. Rocha-Rinza "Hydrogen bond cooperativity and anticooperativity within the water hexamer" *Phys. Chem. Chem. Phys.* **18**, 19557 (2016).

3. E. Francisco, J. L. Casals-Sainz, T. Rocha-Rinza, A. Martín-Pendás "Partitioning the DFT exchange-correlation energy in line with the interacting quantum atoms approach" *Theor. Chem. Acc.*, **135**, 170, (2016).

4. I. Ruiz, E. Matito, F. J. Holguín-Gallego, E. Francisco, Á. Martín Pendás, T. Rocha-Rinza "Fermi and Coulomb correlation effects upon the interacting quantum atoms energy partition" *Theor. Chem. Acc.* **135**, 209, (2016).

5. E. I. Jiménez, W. E. Vallejo-Narváez, C. A. Román-Chavarría, J. Vazquez-Chavez, T. Rocha-Rinza, M. Hernández-Rodríguez "Bifunctional thioureas with α-trifluoromethyl or methyl groups: comparison of catalytic performance on Michael additions" *J. Org. Chem.*, **81**, 7419, (2016).

6. J. M. Guevara-Vela, E. Romero-Montalvo, A. Costales, A. Martín Pendás, T. Rocha-Rinza "The nature of resonance-assisted hydrogen bonds: a quantum chemical topology perspective" *Phys. Chem. Chem. Phys.* **18**, 26383 (2016).

7. E. Romero-Montalvo, J. M. Guevara-Vela, A. Costales, A. Martín Pendás, T. Rocha-Rinza "Cooperative and anticooperative effects in resonance assisted hydrogen bonds in merged structures of malondialdehyde" *Phys. Chem. Chem. Phys.* **19**, 97 (2017).

Lista de alumnos graduados

Durante el periodo reportado, se graduaron los siguientes estudiantes dentro del grupo de trabajo.

- Licenciatura
  - Marco Antonio Tlatelpa Iglesias "Topología de la densidad electrónica en complejos $[M(CO)_n]^q$, con M= Co, Fe; n = 3, 4 y 5 en estado formal de oxidación q= 0, -1, -2 y -3.". Licenciatura en Química, Facultad de Química, UNAM. Examen profesional realizado el 21 de octubre de 2016.
  - Arturo Sauza de la Vega "Topología de la densidad electrónica y análisis de interacciones no covalentes en deshidroalaninas relevantes en química medicinal". Licenciatura en Ingeniería Química Industrial, Escuela Superior de Ingeniería Química e Industrias Extractivas, IPN. Examen profesional realizado el 14 de diciembre de 2016.
- Maestría
  - Eduardo Alejandro Romero Montalvo "Estudio teórico de efectos cooperativos y anticooperativos de enlaces de hidrógeno asistidos por resonancia". Maestría en Ciencias Químicas, UNAM. Examen de grado realizado el 13 de mayo de 2016.

Lista de congresos nacionales e internacionales y participantes.

- Tomás Rocha Rinza "Some developments of quantum chemical topology and their applications to the study of H-bond in ground and excited states", 9th International Society for Theoretical Chemical Physics Conference, Grand Forks, North Dakota, United States of America, del 17 al 22 de julio de 2016.

- Arturo Sauza de la Vega, Tomás Rocha Rinza "Topology of the electron density and noncovalent interactions analysis in relevant dehydroalanines in medicinal chemistry", Frontiers in Computational Chemistry, Ciudad de México, 24 y 25 de agosto de 2016.

- Wilmer Esteban Vallejo Narváez, Tomás Rocha Rinza "A Combined Theoretical and Experimental Study of Amides and Imides Dimerization", Frontiers in Computational Chemistry, Ciudad de México, 24 y 25 de agosto de 2016.

- Arturo Sauza de la Vega, Tomás Rocha Rinza "Topología de la densidad electrónica y análisis de interacciones no covalentes en deshidroalaninas", XV Reunión Mexicana de Fisicoquímica Teórica, Mérida, Yucatán, México, del 17 al 19 de noviembre de 2016.

- Wilmer Esteban Vallejo Narváez, Tomás Rocha Rinza, Marcos Hernández Rodríguez "Estudio teórico-experimental de las interacciones presentes en dímeros de amidas e imidas", XV Reunión Mexicana de Fisicoquímica Teórica, Mérida, Yucatán, México, del 17 al 19 de noviembre de 2016.

Finalmente, se anexan los documentos probatorios de los productos entregables mencionados en este reporte.

Referencias

[1] F. J. Holguín-Gallego, R. Chávez-Calvillo, M. García-Revilla, E. Francisco, Á. Martín-Pendás and T. Rocha-Rinza "Electron correlation in the interacting quantum atoms partition via coupled cluster lagrangian densities" *J. Comput. Chem.* **37**, 1753 (2016).

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[6] J. M. Guevara-Vela, E. Romero-Montalvo, A. Costales, A. Martín Pendás, T. Rocha-Rinza "The nature of resonance-assisted hydrogen bonds: a quantum chemical topology perspective", *Phys. Chem. Chem. Phys.* **18**, 26383 (2016).

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[10] E. Francisco, A. Martín Pendás Imolint: University of Oviedo (unpublished)

[11] E. Francisco, A. Martín Pendás Promolden: A QTAIM/IQA code University of Oviedo (unpublished)

Electron Correlation in the Interacting Quantum Atoms Partition via Coupled-Cluster Lagrangian Densities

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The electronic energy partition established by the Interacting Quantum Atoms (IQA) approach is an important method of wavefunction analyses which has yielded valuable insights about different phenomena in physical chemistry. Most of the IQA applications have relied upon approximations, which do not include either dynamical correlation (DC) such as Hartree-Fock (HF) or external DC like CASSCF theory. Recently, DC was included in the IQA method by means of HF/Coupled-Cluster (CC) transition densities (Chávez-Calvillo et al., *Comput. Theory Chem*. 2015, *1053*, 90). Despite the potential utility of this approach, it has a few drawbacks, for example, it is not consistent with the calculation of CC properties different from the total electronic energy. To improve this situation, we have implemented the IQA energy partition based on CC Lagrangian one- and two-electron orbital density matrices. The development presented in this article is tested and illustrated with the H_2, LiH, H_2O, H_2S, N_2, and CO molecules for which the IQA results obtained under the consideration of (i) the CC Lagrangian, (ii) HF/CC transition densities, and (iii) HF are critically analyzed and compared. Additionally, the effect of the DC in the different components of the electronic energy in the formation of the T-shaped $(H_2)_2$ van der Waals cluster and the bimolecular nucleophilic substitution between F^- and CH_3F is examined. We anticipate that the approach put forward in this article will provide new understandings on subjects in physical chemistry wherein DC plays a crucial role like molecular interactions along with chemical bonding and reactivity. © 2016 Wiley Periodicals, Inc.

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Introduction

Quantum chemical topology (QCT)[1] constitutes an important set of tools for wavefunction analyses.[1–7] Of special interest to this work is the fact that QCT has served as the basis to electronic energy decompositions such as the one derived from the Quantum Theory of Atoms in Molecules (QTAIM)[8] and the Chemical Energy Component Analysis (CECA), the latter allowing to divide the Hartree-Fock (HF) energy in one- and two-electron contributions.[9,10] The Interacting Quantum Atoms (IQA)[11,12] is an electronic energy partition built on the reduced first order density matrix, $\varrho_1(\mathbf{r}_1, \mathbf{r}_1')$ and the pair density $\varrho_2(\mathbf{r}_1, \mathbf{r}_2)$,[13,14] and it has become an important method within QCT. The IQA approach has given valuable insights about different relevant systems and phenomena in chemistry such as bonding in diatomic molecules,[11,12,15–18] noncovalent interactions,[18–22] and isomerization and dissociation reactions.[17,18,21]

From its beginning,[11] the IQA energy partition was implemented along with the *ab initio* (i) HF (equivalent to the CECA approach), (ii) complete active space self-consistent field, and (iii) full (FCI) and truncated configuration interaction wavefunction approximations. While both the monoconfigurational and multiconfigurational self consistent field methods are unable to substantially recover the effects of dynamical correlation (DC), the FCI methodology is rarely achievable due to its prohibitive computational cost and truncated CI is not size consistent. There have been different attempts to incorporate DC in the IQA energy partition, for example, through the consideration of one- and two-atom components of Kohn-Sham density functional theory energies.[23,24] In a different approach to include DC in the IQA energy partition, Chávez-Calvillo et al. in Ref. [25] (hereafter referred as article I) considered HF/Coupled-Cluster (CC) transition density matrices,[26]

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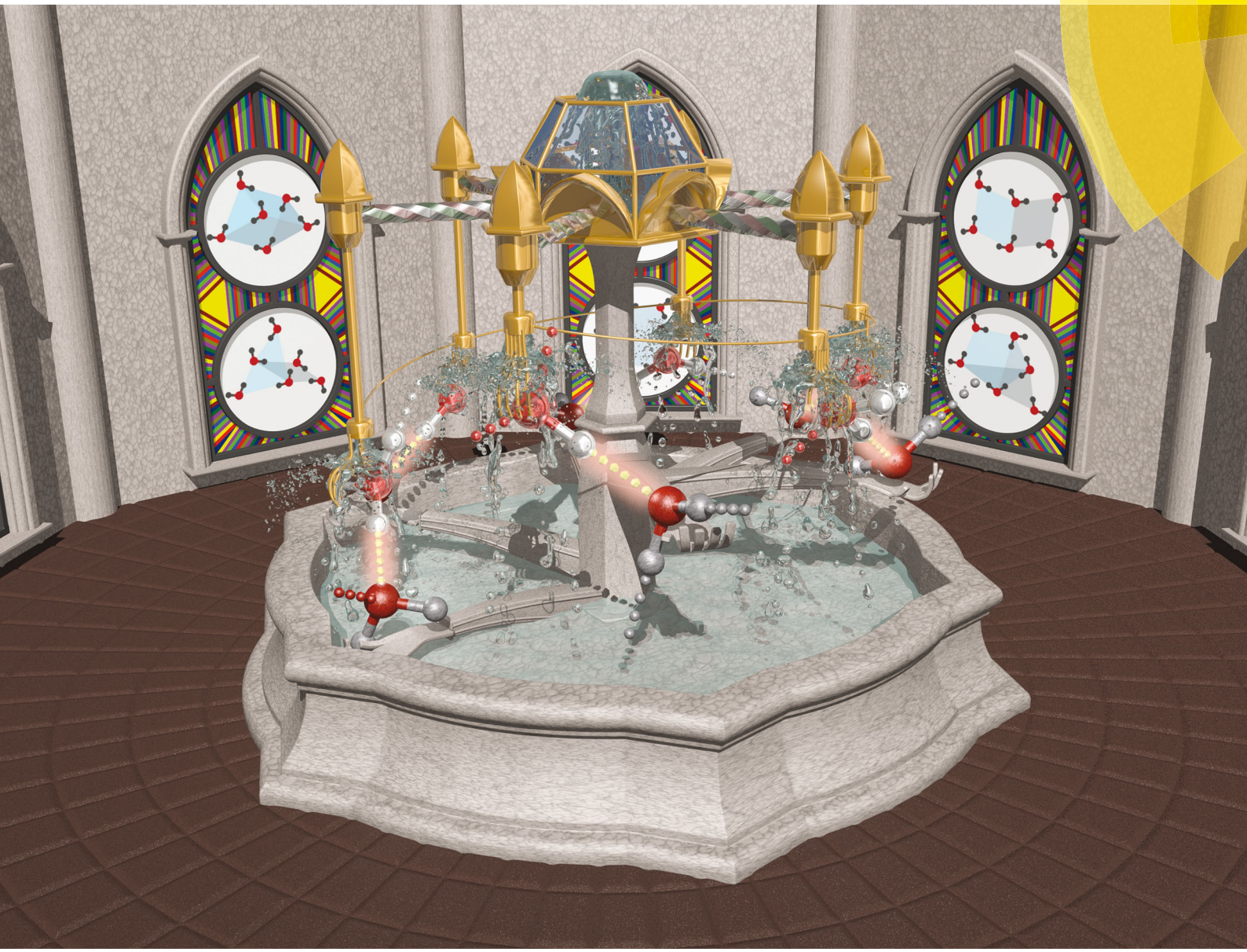

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Hydrogen bond cooperativity and anticooperativity within the water hexamer

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Hydrogen bond cooperativity and anticooperativity within the water hexamer

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The hydrogen bond (HB), arguably the most important non-covalent interaction in chemistry, is getting renewed attention particularly in materials engineering. We address herein HB non-additive features by examining different structures of the water hexamer (cage, prism, book, bag and ring). To that end, we rely on the interacting quantum atoms (IQA) topological energy partition, an approach that has been successfully used to study similar effects in smaller water clusters (see *Chem. – Eur. J.*, **19**, 14304). Our IQA interaction energies, $\left|E_{\mathrm{int}}^{\mathrm{H_2O\cdots H_2O}}\right|$, are used to classify the strength of HBs in terms of the single/double character of the donor and acceptor H_2O molecules involved in the interaction. The strongest hydrogen bonds on this new scale entail double donors and acceptors that show larger values of $\left|E_{\mathrm{int}}^{\mathrm{H_2O\cdots H_2O}}\right|$ than those observed in homodromic cycles, paradigms of cooperative effects. Importantly, this means that besides the traditional HB anticooperativity ascribed to double acceptors and donors, the occurrence of these species is also related to HB strengthening. Overall, we hope that the results of this research will lead to a further understanding of the HB non-additivity in intramolecular and intermolecular interactions.

1 Introduction

The hydrogen bond (HB) is among the most important intermolecular interactions in chemistry. For example, the HB is the source of the unique properties of water, both in pure form and as a solvent,[1–3] and its significance has been recognised in a broad variety of systems and phenomena in biochemistry[4–6] and supramolecular chemistry[7–9] among other fields. Additionally, the HB has gotten renewed interest due to its involvement in the development of lithium-based batteries[10,11] and more generally in crystal and materials engineering.[12–14]

A major feature of HB interactions is their non-additive character, which results from contributions to the interaction energy such as covalence, polarization, and charge transfer. Two hydrogen bonds may strengthen or weaken each other:[15,16] these two opposite situations are commonly referred to as HB cooperative and anticooperative effects, respectively.[17] The former are usually related to HB chains in which the hydrogen bonds point along the same direction, *e.g.* HB sequences like A–H···B–H···C–H···, or homodromic cycles as that shown in Fig. 1(a).[17] On the other hand, anticooperative effects are normally associated with systems comprising double donors (A···H–B–H···C) or double acceptors (A–H···B···H–C), for example, those present in antidromic cycles, displayed in Fig. 1(b).[16,17]

Water clusters have widely become an archetype in the study of non-additivity in hydrogen bonding, particularly as cooperativity

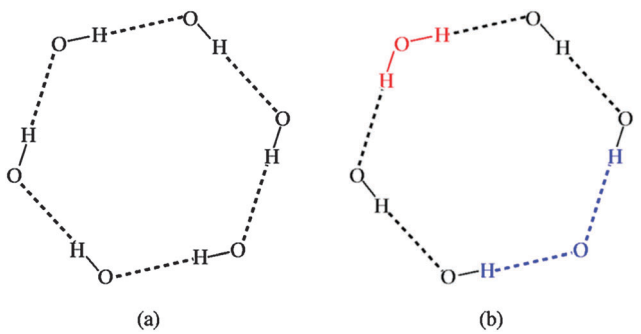

Fig. 1 (a) Homodromic and (b) antidromic cycles of hydrogen bonding networks. The double H-bond donor (acceptor) is highlighted in red (blue).

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understanding of the critical role played by cooperativity and anticooperativity in the determination of the structure of hydrogen-bonded molecular clusters.

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REGULAR ARTICLE

Partitioning the DFT exchange-correlation energy in line with the interacting quantum atoms approach

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Abstract The interacting quantum atoms (IQA) energy partition has given important insights about different systems and processes in theoretical chemistry. Given its intrinsic dependence on first- and second-order density matrices, IQA is only cleanly defined within wavefunction methods. This means that, despite the importance of density functional theory (DFT) in electronic structure methods, a neat IQA–DFT implementation is not straightforward. This work addresses this issue through a new implementation of IQA within the Kohn–Sham formalism of DFT in conjunction with hybrid and non-hybrid functionals that contributes further to that already presented (Maxwell et al. in Phys Chem Chem Phys, 2016. doi:10.1039/C5CP07021J). For this purpose, we use additive exchange-correlation (xc) energies, defined within the IQA approach, to scale the one- and two-atom terms of the Kohn–Sham xc energy. This leads to an exact partition of the xc DFT energy of a molecule into intra-atomic and inter-atomic contributions. The suggested method is illustrated with several molecules together with some of the most popular local and hybrid DFT functionals. Overall, we anticipate that the approach put forward in this work will prove useful in getting further insights of phenomena in chemistry which are properly described with DFT .

Keywords Energy partition · Density functional theory · Interacting quantum atoms · Quantum theory of atoms in molecules

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1 Introduction

Energy decomposition analyses (EDAs) are essential ingredients in the chemical interpretation of the electronic structure (ES) of molecular systems. Actually, we have come to the paradoxical situation that it is easier to set up and run a calculation using any of the plethora of available ES computer packages, than analyze and extract chemically meaningful information from their outputs. This *status quo* is also found if we descend to the interpretation techniques themselves, where a zoo of methods emerge [1–19].

It is our opinion that the interacting quantum atoms approach (IQA) [20, 21] provides a meaningful EDA that: (1) is compatible with both orbital and real space chemical bonding techniques, (2) is orbital invariant, providing results that do not depend on the underlying ES method and (3) gives rise to physically rooted energetic components with precise, clear meaning. In IQA, all the physical components of the energy of a molecular system (kinetic, electron–nucleus, electron–electron, nucleus–nucleus) are first partitioned according to their one- or two-body character and then divided into one- and two-center (atomic) contributions. To do so, the first (1RDM) and second (2RDM)

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includes both exchange and correlation energy components, whereas $E_x^{AB,KS}$ only has exchange energy since these inter-atomic components are obtained from the KS determinant. In other words, within the AIMALL partition, the correlation energy of the molecule is distributed exclusively between the intra-atomic contributions. Thus, the AIMALL E_{xc}^{AA} values in Table 3 are always more negative than the $\tilde{E}_{xc}^{AA}$ data put forward in this work, and even more negative than the $E_x^{AA,KS}$ numbers, with the last mentioned lacking correlation energy contributions. Conversely, every AIMALL inter-atomic energy E_{xc}^{AB}(AIMALL) is less negative than the corresponding $\tilde{E}_{xc}^{AB}$. We believe that the proposed energy partition of this work is more balanced than that used by AIMALL. It is also less contrived, since both the correlation energy, as well as the exchange energy are distributed into intra- and inter-atomic contributions on the same footing.

5 Conclusions and perspectives

A new heuristic real space partitioning of the DFT exchange-correlation energy into intra- and interatomic terms has been proposed. With this, the total energy of a molecular system described at any standard Kohn–Sham DFT level may be exactly decomposed in the light of the interacting quantum atoms (IQA) approach. Our proposal is based on using the additive atomic exchange-correlation energies as obtained from integrating DFT functionals over IQA atomic regions. These energies are then used to scale the one- and two-atom Kohn–Sham exchange energies coming from a standard IQA calculation performed with a Kohn–Sham determinant. At variance with another recent proposal [23], both the intra- and inter-atomic xc energies are modified by the scaling procedure. As shown in different systems, our results are chemically meaningful and easy to interpret. Armed with this scheme, IQA insights in medium sized molecules should now be feasible. We should not forget, however, that in standard KS-DFT the xc energy also includes the correlation part of the kinetic energy, T_c. Indeed, the cornerstone of the KS approach is the substitution of the system of interacting electrons by an auxiliary set of non-interacting particles that exhibit the exact interacting density, and whose kinetic energy (T_s) is exactly obtained from the KS determinant. In this sense, our decomposed xc energies will also include T_c, and our atomic kinetic energies will only contain the non-interacting kinetic energy of the Kohn–Sham system. We are working on how to appropriately correct the non-interacting kinetic energies [40].

Finally, we would like to point out that we do not claim in this article that a KS-DFT IQA method can offer a route to perform an IQA analysis safer than that provided by a post-HF wavefunction method. Instead, this paper deals with a major problem on the application of the IQA partition energy based on a previous DFT calculation. This type of IQA analyses, as it occurred in the past with delocalization indices, are being obtained directly from KS determinants without any consideration of correlation corrections in such a way that the total DFT energy is not recovered. Being aware of this fact, we tried in this work to provide a plausible route to extract the IQA quantities (which many times before have shown their usefulness in the analysis of the chemical bond in a wide variety of molecules and molecular clusters) from KS-DFT wavefunctions conserving the total KS-DFT energy. We are sure that these quantities will outperform those obtained naïvely from KS determinants.

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REGULAR ARTICLE

Fermi and Coulomb correlation effects upon the interacting quantum atoms energy partition

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Abstract The Interacting Quantum Atoms (IQA) electronic energy partition is an important method in the field of quantum chemical topology which has given important insights of different systems and processes in physical chemistry. There have been several attempts to include Electron Correlation (EC) in the IQA approach, for example, through DFT and Hartree–Fock/coupled-cluster (HF/CC) transition densities. This work addresses the separation of EC in Fermi and Coulomb correlation and its effect upon the IQA analysis by taking into account spin-dependent one- and two-electron matrices $D^{\mathrm{HF/CC}}_{p\sigma q\sigma}$ and $d^{\mathrm{HF/CC}}_{p\sigma q\sigma r\tau s\tau}$ wherein σ and τ represent either of the α and β spin projections. We illustrate this approach by considering BeH_2, BH, CN^-, HF, LiF, NO^+, LiH, $H_2O\cdots H_2O$ and HC≡CH, which comprise non-polar covalent, polar covalent, ionic and hydrogen bonded systems. The same and different spin contributions to (1) the net, interaction and exchange-correlation IQA energy components and (2) delocalisation indices defined in the quantum theory of atoms in molecules are carefully examined and discussed. Overall, we expect that this kind of analysis will yield important insights about Fermi and Coulomb correlation in covalent bonding, intermolecular interactions and electron delocalisation in physical chemistry.

Keywords Interacting quantum atoms · Fermi and Coulomb correlation · Spin-dependent one and two-electron matrices · Delocalisation indices · HF/CC transition densities

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1 Introduction

Wavefunction analyses are aimed to get chemical insights from electronic structure calculations. Unfortunately, there are many concepts in chemistry e.g. aromaticity, chemical bonds, electron delocalisation and atomic charges which are not observables [1]. Hence, there is no an unique way to compute quantities related with such intuitive chemical notions. For example, there are orbital-based approaches such as Mulliken [2] and Löwdin [3] population schemes which have been developed for the calculation of atomic charges in molecular and supramolecular systems. Nonetheless, these techniques have the disadvantage of being very dependent on the particular elements used to build the wavefunction like the basis set [4].

Instead, it is preferable to examine the information contained in the state vector by means of the study of an observable computed from it. Methods in quantum chemical topology (QCT), for instance, the Quantum Theory of Atoms in Molecules (QTAIM) [5] and the Interacting

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and $\delta^{\mathrm{N,O}}_{\sigma\tau,\mathrm{CISD}} = -0.538$). These numbers put forward that the HF/CC cross-spin pair density expressions underestimate Coulomb correlation to some extent. Overall, we can safely conclude that HF/CC pair density expressions are adequate to describe ionic and weak interaction molecules but underestimate the Coulomb correlation effects in covalent bonds, leading to an overestimation of DI.

A better consideration of DC in delocalisation indices by means of coupled-cluster theory warrants further investigation in approximated CC density matrices.

7 Concluding remarks

We have considered spin-dependent one- and two- electron matrices based on HF and HF/CC transition densities to evaluate separately the Fermi and Coulomb correlations consequences on the IQA electronic energy partition. The results show that the net unlike-spin correlation is the dominant factor in the reduction of the electron–electron repulsion across the system to the extent that in some cases it surpasses the decrease in V_{ee} in the whole molecule or molecular cluster. This situation leads to an increase in the electronic repulsion among the QTAIM basins. Overall, different Fermi and Coulomb correlations effects are observed in the IQA net and interaction energies. The same spin-dependent density matrices were used to determine the impact of these two types of correlation in QTAIM delocalisation indices. Our results show that although $\rho_2^{\mathrm{HF/CC}}(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_1^{\mathrm{HF/CC}}(\mathbf{r}_1; \mathbf{r}_1')$ in conjuntion can give a proper account of electron correlation on the DIs, care must be taken in the consideration of approximations based only on the latter scalar field. Altogether, we expect that the approach presented in this work prove useful in the evaluation of Fermi and Coulomb effects both in quantum chemical topology and to benchmark the Fermi and Coulomb holes in the framework of density functional development.

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Bifunctional Thioureas with α-Trifluoromethyl or Methyl Groups: Comparison of Catalytic Performance in Michael Additions

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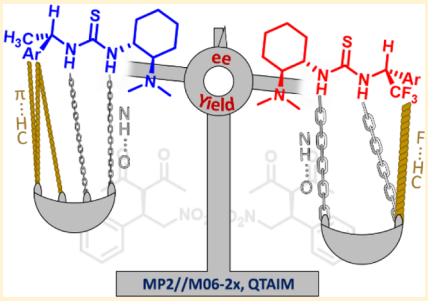
Supporting Information

ABSTRACT: Thioureas are an important scaffold in organocatalysis because of their ability to form hydrogen bonds that activate substrates and fix them in a defined position, which allows a given reaction to occur. Structures that enhance the acidity of the thiourea are usually used to increase the hydrogen-bonding properties, such as 3,5-bis(trifluoromethyl)phenyl and boronate ureas. Herein, we report the synthesis of bifunctional thioureas with a chiral moiety that include either a trifluoromethyl or methyl group. Their catalytic performance in representative Michael addition reactions was used in an effort to compare the electronic effects of the fluorination at the methyl group. The observed differences concerning yields and ee values cannot be attributed solely to the different steric environments; theoretical results indicate distinct interactions within the corresponding transition states. The calculated transition states show that the fluorinated catalysts have stronger N−H···O and C−H···F hydrogen bonds, while the nonfluorinated systems have C−H···π contacts. These results have shown that a variety of hydrogen-bonding interactions are important in determining the yield and selectivity of thiourea organocatalysis. These details can be further exploited in catalyst design.



INTRODUCTION

Hydrogen-bonding catalysis and a chiral counterion strategy have risen recently as a reliable synthetic methodology.[1] Takemoto[2] introduced chiral bifunctional catalysts[3] to activate an electrophile through hydrogen bonds (HB). These systems also contain a tertiary amine that deprotonates a nucleophile which is subsequently added. The Takemoto catalyst (Figure 1a) features a

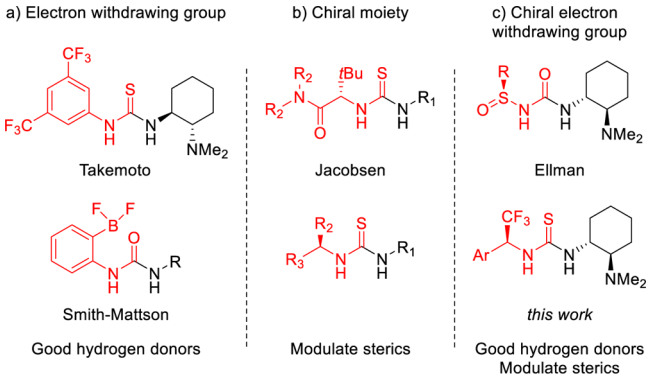


Figure 1. Moieties used to enhance hydrogen bond donor properties or to modulate steric effects in H-bond catalysis and counterion strategies.

3,5-bis(trifluoromethyl)phenyl group[4] that enhances the acidity of the thiourea and thereby increases its hydrogen-bonding properties. Boronate ureas have a similarly enhanced HB donor capacity of the HNC(O) moiety, in this case by means of an internal Lewis acid.[5,6] Stereocontrol of the addition products[7] can be achieved by addition of chiral substituents to the thiourea moiety (Figure 1b); however, this is done at the expense of the HB activation ability. Nonetheless, if a chiral group with electron-withdrawing properties is bound to the thiourea (Figure 1c), a good compromise between the modulation of the steric demands and activation by the catalyst can be accomplished. On this subject, Ellman,[8] Jacobsen, and others[9] have used *N*-sulfinyl ureas that are able to catalyze a variety of reactions. Herein we report the synthesis and application of bifunctional thioureas with a chiral group that incorporates a trifluoromethyl group in its structure.[10] Thioureas featuring trifluoromethyl groups have shown exceptional properties in the recognition of chiral carboxylates with binding constants that are 10 times higher than those for the analogous nonfluorinated compounds.[11] The chiral moiety with $-CF_3$ confers to the thioureas reported in this work (1) good HB properties[12] without the deactivation of the catalyst by intramolecular interactions[13] and (2) the possibility of modulating the steric environment. In addition, the catalysts put forward in this are easily synthesized and allow the incorporation of a variety of functional groups in their structure. This study also considers the corresponding nonfluorinated catalysts[14] to provide insights into the effect of the NH acidity on the yield and enantiomeric excess of the reactions considered in this investigation.

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HPLC: Chiralcel OJ, hexane/ethanol 70/30, 0.8 mL/min, λ 220 nm, retention times 22.2 min (*S*), 41.4 (*R*).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01063.

Kinetics of the addition of 2,4-pentanodione to β-nitrostyrene and QTAIM analysis of the transition states with catalysts **5a**−**8a**, Takemoto's and Pápai's calculated mechanisms with catalyst **6a**, ^{1}H and ^{13}C NMR spectra of compounds obtained in this work, HPLC traces, and Cartesian coordinates and energies of computed structures (PDF)

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Notes

The authors declare no competing financial interest.

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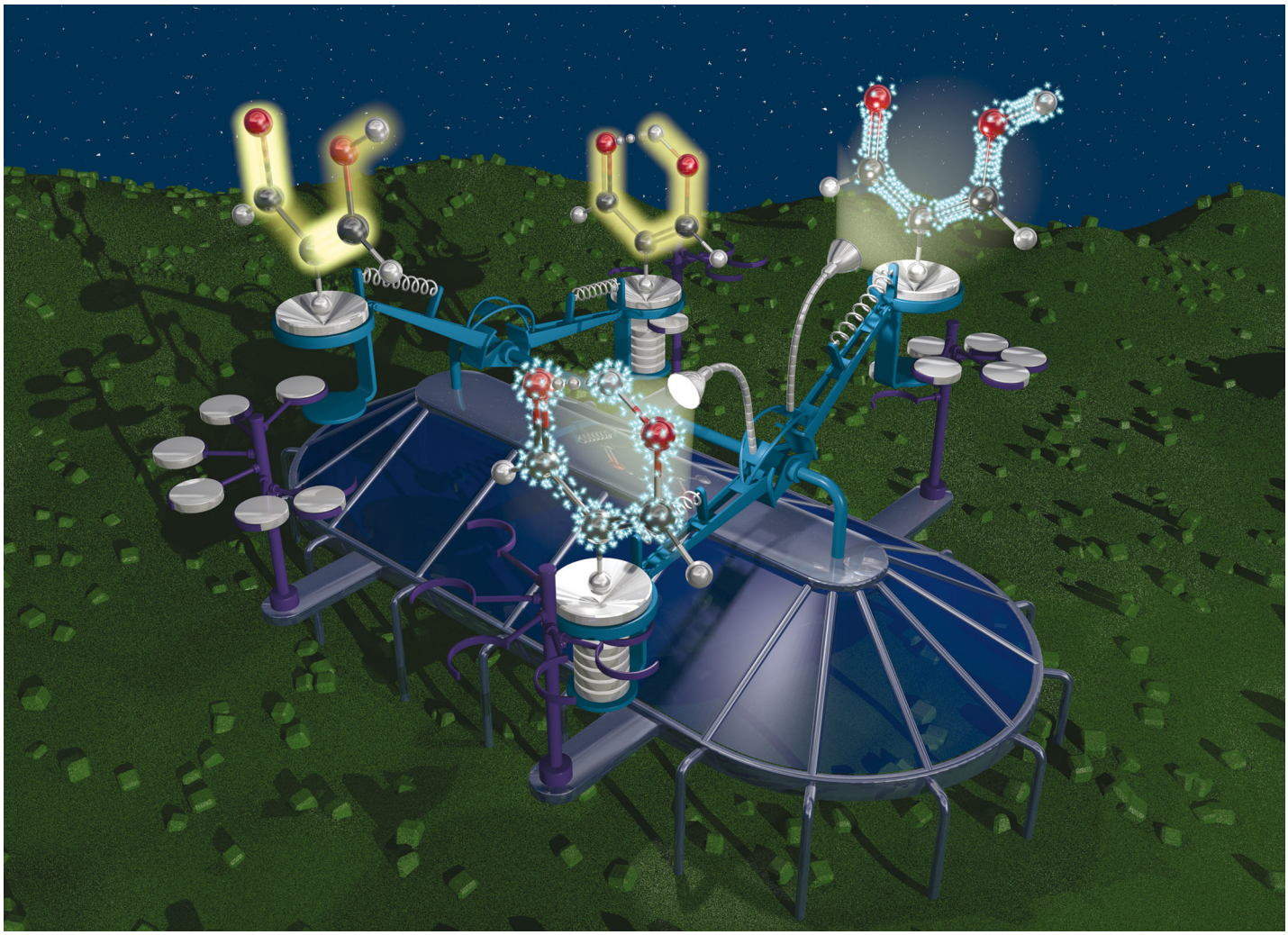

Showcasing the work at the Departments of Physical Chemistry at the Institute of Chemistry/UNAM and the University of Oviedo

Title: The nature of resonance-assisted hydrogen bonds: a quantum chemical topology perspective

This work addresses the nature of Resonance Assisted Hydrogen Bonds (RAHBs) by considering malonaldehyde whose H-bonded (closed) and non H-bonded (open) conformations are represented in the bottom and top of the seesaws respectively. Although delocalization indices are more uniform in the closed form (seesaw in the left), the number of delocalized electrons diminish on RAHB formation. The interaction is characterized by an increase/decrease in the intra-atomic/inter-atomic exchange energies as schematized with sparks in the highlighted seesaw in the right. The artwork is due to Mr Víctor Duarte Alaniz.

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The nature of resonance-assisted hydrogen bonds: a quantum chemical topology perspective†

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Resonance Assisted Hydrogen Bonds (RAHBs) are particularly strong H-Bonds (HBs) which are relevant in several fields of chemistry. The traditional explanation for the occurrence of these HBs is built on mesomeric structures evocative of electron delocalisation in the system. Nonetheless, there are several theoretical studies which have found no evidence of such electron delocalisation. We considered the origin of RAHBs by employing Quantum Chemical Topology tools, more specifically, the Quantum Theory of Atoms in Molecules (QTAIM) and the Interacting Quantum Atoms energy partition. Our results indicate that the π-conjugated bonds allow for a larger adjustment of electron density throughout the H-bonded system as compared with non-conjugated carbonyl molecules. This rearrangement of charge distribution is a response to the electric field due to the H atom involved in the hydrogen bonding of the considered compounds. As opposed to the usual description of RAHB interactions, these HBs lead to a larger electron localisation in the system, and concomitantly to larger QTAIM charges which in turn lead to stronger electrostatic, polarization and charge transfer components of the interaction. Overall, the results presented here offer a new perspective on the cause of strengthening of these important interactions.

1 Introduction

Hydrogen bonds (HBs) play a fundamental role in structural chemistry and biology.[1,2] Because of their mid-range strength and strong directionality, HBs are crucial in determining the structure and dynamics of a great diversity of molecular clusters and assemblies. For instance, the formation and dissociation of HBs at room temperature gives them an important role in many biochemical processes.[3]

Although a large amount of work has been developed to comprehend the essential features of H-bonds, many controversies still persist on this issue. For many authors the interaction is mainly electrostatic,[1,2,4,5] while others describe it as partially covalent.[6–12] Indeed, H-bonding is a very complex interaction which includes a wide variety of species and energy ranges: the formation energies of H-bonds cover the range from 0.2 to 40 kcal mol^{-1}.[13] Resonance assisted hydrogen bonds (RAHBs) are particularly strong HBs in uncharged molecules.[13,14] Since Gilli *et al.*[14–16] proposed the concept of RAHBs, this has had great success in many fields such as organic chemistry,[17–21] infrared spectroscopy,[22] nuclear magnetic resonance,[23] electron diffraction,[24] or biological chemistry.[25–28]

The proton donor and proton acceptor groups in RAHBs are connected through a chain of π-conjugated double bonds, and the standard explanation of the noticeable strength of these interactions is based on a chemically intuitive reasoning in which the conjugated bonds display an equalization of lengths through a pseudo-ring. This description of RAHBs is consistent with the deeply rooted idea that the existence of equivalent resonance structures is a stabilizing feature of a molecular system. As Fig. 1 shows, the tautomeric structures of malonaldehyde, an archetypal RAHB system, are evocative of a transfer of electron density in which the hydrogen bond acceptor turns into the hydrogen bond donor and *vice versa*.

Despite this chemically appealing explanation of RAHBs, many computational chemistry studies have failed so far to give indications of the presumed correlation between the amount of electron delocalisation and the energetics of these interactions. For example, the substitution of electron donating and withdrawing

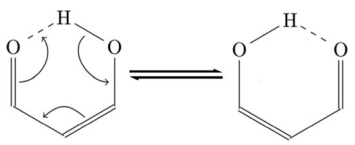

Fig. 1 Tautomeric structures related to the resonance assisted hydrogen bond in malonaldehyde.

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distinctive feature of the stabilization mediated by conjugation in RAHBs. A major insight results from the observation that such alternation is mostly absent in the saturated systems (c) and (d). As expected, covalent conjugation effects are not found in the saturated molecules. In all cases the formation of the H-bond makes the corresponding X–H bond less covalent ($\Delta V_{x}^{X-H} > 0$) and more ionic ($\Delta V_{cl}^{X-H} < 0$), a fact that supports the superior contribution of electrostatics over covalency in these systems. Similar insights can be obtained for the rest of the ring bonds. Finally, we emphasize that the changes in all the energetic components are overall larger in magnitude for the conjugated compounds, in line with the larger charge density flow allowed by the π channels.

5 Conclusions

We have considered the origin of the RAHB interaction by means of quantum chemical topology. Our results indicate that the electric field due to the bridging hydrogen induces a strong redistribution of the electron density in the conjugated molecules CHO–CH═CH–OH and CHO–CH═CH–NH_2, which leads to a decrease in the electron delocalisation within the system as opposed to the usual explanation of the resonance assisted H-bonds. Indeed, the intra-atomic exchange contribution of the electron energy increases at the expense of the corresponding interatomic counterpart. The IQA and QTAIM analyses indicate that the π channels of the analyzed conjugated carbonyls allow for a greater reorganization of the one and two-electron distributions which lead to important contributions from electrostatics, polarization and charge transfer in the establishment of an RAHB. On the whole, we anticipate that the new interpretation of the resonance assisted hydrogen bonds presented herein will prove valuable in the understanding of these important interactions in different fields of physical chemistry.

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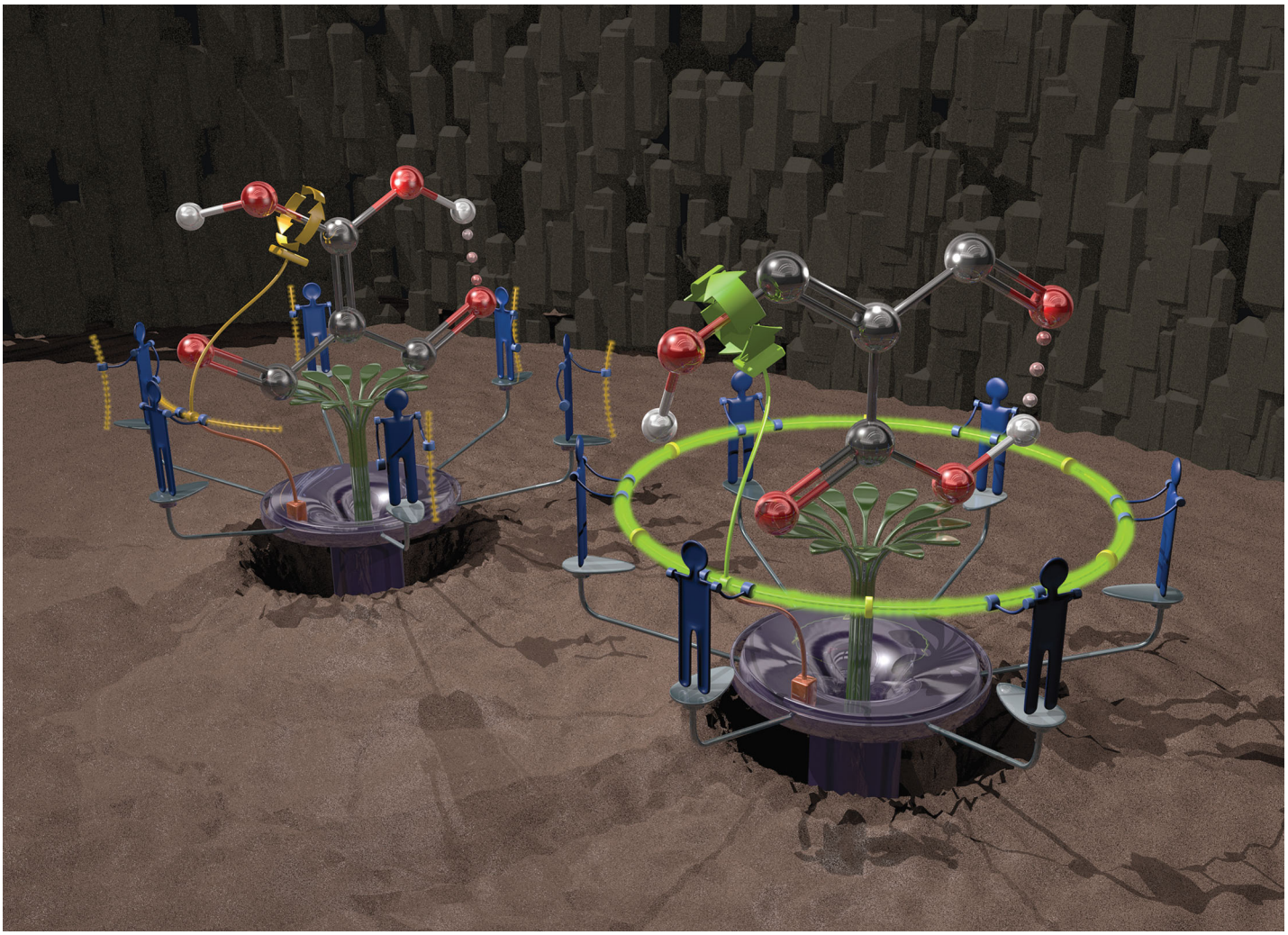

Showcasing work from the Department of Physical Chemistry at the Institute of Chemistry/UNAM and the University of Oviedo

Cooperative and anticooperative effects in resonance assisted hydrogen bonds in merged structures of malondialdehyde

We investigated H-bond cooperative and anticooperative effects occuring throughout the network of π-bonds in different β-enolones by means of potential energy curves and quantum chemical topology (QCT). The mesomeric structures are consistent with the determined cooperativity (right) and anticooperativity (left) of these interactions represented with joined green light and separated yellow staffs respectively. QCT analyses showed that the investigated H-bonds have a strong effect on the surrounding π system. Indeed these H-bond non-additive effects are associated with different strengthening of the pseudo-bicyclic structures examined in this research.

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Cooperative and anticooperative effects in resonance assisted hydrogen bonds in merged structures of malondialdehyde†

Eduardo Romero-Montalvo,[a] José Manuel Guevara-Vela,[b] Aurora Costales,[b] Ángel Martín Pendás[b] and Tomás Rocha-Rinza*[a]

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We analyzed non-additive effects in resonance assisted hydrogen bonds (RAHBs) in different β-enolones, which are archetypal compounds of these types of interactions. For this purpose, we used (i) potential energy curves to compute the formation energy, $\Delta E_{\text{form}}^{\text{RAHB}}$, of the RAHBs of interest in different circumstances along with (ii) tools offered by quantum chemical topology, namely, the Quantum Theory of Atoms In Molecules (QTAIM) and the Interacting Quantum Atoms (IQA) electronic energy partition. We established the effect that a given H-bond exerts over $\Delta E_{\text{form}}^{\text{RAHB}}$ associated with another RAHB, determining in this way the cooperativity or the anticooperativity of these interactions. The mesomeric structures and the QTAIM delocalisation indices are consistent with the determined cooperative or anticooperative character of two given RAHBs. The HB cooperativity and anticooperativity studied herein are directly reflected in the IQA interaction energy $E_{\text{int}}^{\text{O}\cdots\text{H}}$, but they are modulated by the surrounding hydrocarbon chain. The IQA decomposition of ΔE_{coop}, a measure of the cooperativity between a pair of interacting RAHBs, indicates that the analyzed H-bond cooperative/anticooperative effects are associated with greater/smaller (i) strengthening of the pseudo-bicyclic structure of the compounds of interest and (ii) electron localisations with its corresponding changes in the intra and intermolecular exchange–correlation contributions to $\Delta E_{\text{form}}^{\text{RAHB}}$. Overall, we expect that this investigation will provide valuable insights into the interplay among hydrogen bonded atoms and the π system in RAHBs contributing in this way to the understanding of the general features of H-bonds.

1 Introduction

Since its discovery in the 1920s[1] many different experimental and theoretical investigations have been dedicated to the hydrogen bond (HB). The importance of this interaction resides not only on its effects on diverse systems in chemistry and biology but also on its complexity. For instance, the energetics of an O–H···O H-bond might lie in the range of 1–30 kcal mol^{-1}.[2] Further problems in the characterization of HBs arise from the dissimilar proportions of their covalent, electrostatic and dispersion contributions.[3] This situation has led to the coinage of the term "H-bond puzzle" to indicate the lack of an overall H-bond model to predict the structure and energetics from the chemical formulae of the interacting fragments, as opposed to, for example, Lewis' electron pair theory. Indeed, the intricate character of the HB makes it very versatile and ubiquitous in many processes: from giving water its extraordinary features[4] to the HB involvement in complicated biochemical reactions[5] among other phenomena.

Part of the difficulty in the understanding of the HB originates in its non-additivity. Apart from the electrostatic component in non-covalent interactions, the distinct contributions to the HB formation energy are non-additive,[6] *i.e.*, the value of the component of the interaction energy of two species is affected by the presence of a third electronic system, which leads to cooperative and anticooperative effects of the HB. The former occurs when hydrogen bonds strengthen each other whereas the latter involves a mutual weakening of the interactions. For example, the HBs in a linear structure of the type BH···BH···BH, like that shown in Fig. 1(a), display cooperative effects[7] as opposed to those present in a double hydrogen bond donor (Fig. 1(b)), which exhibit HB anticooperativity. The charge transfer leading to the referred non-additive effects takes place through σ bonds and hence it is called "σ-bond" cooperativity or anticooperativity.[3]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp04877c

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UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

PROGRAMA DE MAESTRÍA Y DOCTORADO EN CIENCIAS QUÍMICAS

ESTUDIO TEÓRICO DE EFECTOS COOPERATIVOS Y ANTICOOPERATIVOS EN ENLACES DE HIDRÓGENO ASISTIDOS POR RESONANCIA (EHARS)

TESIS

PARA OPTAR POR EL GRADO DE

MAESTRO EN CIENCIAS

PRESENTA

Q. EDUARDO ALEJANDRO ROMERO MONTALVO

Tutor: Dr. Tomás Rocha Rinza, Ciudad de México. Abril de 2016.

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CONSTANCIA DE EXAMEN

100 años Facultad de Química 1916 - UNAM - 2016

Folio F.Q. 3320

Dr. Fernando Cortés Guzmán, secretario del jurado que examinó al alumno EDUARDO ALEJANDRO ROMERO MONTALVO para optar por el grado de MAESTRO EN CIENCIAS, hace constar que obtuvo el siguiente resultado

Aprobado con Mención Honorífica.

Ciudad Universitaria, D.F., a 13 de mayo de 2016

El Secretario del Jurado

FIRMA

Una vez transcurridos 45 días hábiles, el interesado deberá ingresar a la página www.dgae.unam.mx en la opción egreso, para consultar en que situación se encuentra el trámite de su pergamino, o comunicarse a TRAMITEL a los teléfonos 56.22.55.68 al 72. Cuando tenga la indicación del Programa "Tramitel" de presentarse a recoger su Grado, acudir al edificio de la D.G.A.E., en Circuito de la Investigación Científica entre la parada del metro Universidad y el Centro del Desarrollo Infantil (CENDI) en Ciudad Universitaria de 9:00 a 17:00 hrs.

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DR. TOMÁS ROCHA RINZA

SUSTENTANTE:

MARCO ANTONIO TLATELPA IGLESIAS

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VNIVERSIDAD NACIONAL
AVTONOMA DE MEXICO

CONSTANCIA DE EXAMEN

MARCO ANTONIO TLATELPA IGLESIAS
(Nombre del Sustentante)

P r e s e n t e.

En el examen profesional que sustento el día de hoy para obtener el título de

QUIMICO

el jurado ha tenido a bien otorgarle la calificacion de:

APROBADO

Ciudad Universitaria, Cd.Mx., 21 de octubre de 2016

El Secretario del Jurado

Al cabo de 45 días posteriores al Examen Profesional , comuníquese al programa 'Tramitel' cuyos teléfonos son: 56 22 55 68 al 72; para recabar informes sobre su Título, Grado o Diploma, proporcionando nombre y no. de cuenta.
Cuando tenga la indicación por vía telefónica de pasar a recoger su Título, Grado o Diploma, deberá presentarse en el Programa 'Tramitel' ubicado en el edificio de la D.G.A.E., Circuito de la Investigación Científica entre la parada CU del metro Universidad y el Centro de Desarrollo Infantil (CENDI), en Ciudad Universitaria.

Instituto Politécnico Nacional

Escuela Superior de Ingeniería Química e Industrias Extractivas

TOPOLOGÍA DE LA DENSIDAD ELECTRÓNICA Y ANÁLISIS DE INTERACCIONES NO COVALENTES EN DESHIDROALANINAS RELEVANTES EN QUÍMICA MEDICINAL

T E S I S

QUE PARA OBTENER EL TÍTULO DE:

INGENIERO QUÍMICO INDUSTRIAL

PRESENTA:

Arturo Sauza de la Vega

ASESOR

Dr. Tomás Rocha Rinza

ASESOR INTERNO

Ing. José Clemente Reza García

Reconocimientos

- Al Instituto Politécnico Nacional y a la Escuela Superior de Ingeniería Química e Industrias Extractivas, ESIQIE por la oportunidad de estudiar en tan prestigiosas instituciones.
- Para la Universidad Nacional Autónoma de México y al Instituto de Química de la UNAM, por haberme brindado los recursos para el desarrollo de esta tesis así como todas las enseñanzas y aprendizaje que me han dejado.
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PROTESTA

Ante el Honorable Jurado de mi examen profesional, como Ingeniero Egresado de esta Escuela Superior de Ingeniería Química e Industrias Extractivas.

PROTESTO POR MI HONOR

Que ejerceré mi profesión con absoluta honradez, ética, lealtad y decoro, contribuyendo con todo mi empeño y mis facultades al beneficio de la sociedad.

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"LA TÉCNICA AL SERVICIO DE LA PATRIA"

Ciudad de México, a 13 de diciembre del 2016

SUSTENTANTE: ARTURO SAUZA DE LA VEGA

PROGRAM SCHEDULE

CONGRESS OF THE INTERNATIONAL SOCIETY OF THEORETICAL CHEMICAL PHYSICS 2016 CONFERENCE
ALERUS CENTER, 1200 South 42nd Street, Grand Forks, ND, USA
JULY 17-22, 2016

SUNDAY, JULY 17

BALLROOM 5

3:00pm-9:00pm **Registration**

4:00pm-5:00pm **Opening Remarks**

5:00pm-6:00pm **Plenary I** **Chair: M. Hoffmann**
Andreas Savin (CNRS; University of Paris - Sorbonne)
''Multireference Density Functional Theory"

6:00pm-7:00pm **AFTERNOON SESSION** **Chair: P. Gill**
Mixed I
Kenneth Ruud (University of Tromsø)
"Molecular Response Properties in the Relativistic Domain"

Katarzyna Pernal (Lodz University of Technology)
"*Reduced Density Matrix Embedding"*

7:15pm-9:15pm **Welcome Reception**

MONDAY, JULY 18

7:30am-6:00pm **Conference Registration**

8:00am-9:30am **MORNING SESSION A**
BALLROOM 5 **Electronic Structure IA** **Chair: P. Piecuch**
Paul Ayers (McMaster University)
"Geminals-Based Approaches for Strongly Correlated Systems with Open Shells"

Garnet Chan (Princeton University)
"Periodic Quantum Chemistry"

Mihály Kállay (Budapest University of Technology and Economics)
"*Efficient Fragmentation-Based Linear-Scaling CCSD(T) Methods"*

ORIOLE ROOM 2 **Complex Systems IA** **Chair: J. Gao**
Jiali Gao (University of Minnesota)

Heather Kulik (Massachusetts Institute of Technology)
"Quantifying Electronic Effects in Enzyme Active Sites"

Yasuteru Shigeta (University of Tsukuba)
"Efficient Conformational Search Methods for Protein Folding Problems"

PHEASANT ROOM 3 **DFT Subsystems IA** **Chair: J. Neugebauer**
Tomasz Wesolowski (University of Geneva)
"Recent Progress in Density Embedding Theory and its Applications?"

Michele Pavanello (Rutgers University)
"Embedding Ground and Excited States in Real and Imaginary Time"

Claudia Filippi (University of Twente)
"Multiscale Modeling for Excited States: Capturing Polarization in Biomolecules"

9:30am-10:00am **Coffee Break** 

10:00am-11:00am **Plenary II** **Chair: P. Surjan**
BALLROOM 5
Debashis Mukherjee (Indian Association for the Cultivation of Science)
"A Survey of the Unitary Group Adapted MRCC and MRPT Theories: SU vs SS Approaches"

11:00am-12:30pm **MORNING SESSION B**
BALLROOM 5
Electronic Structure IB **Chair: G. Scuseria**
Andreas Köhn (University of Stuttgart)
"Internally Contracted Multireference Coupled-Cluster Theory"

Ron Shepard (Argonne National Laboratory)
"Recent Developments with the Graphically Contracted Function Electronic Structure Method"

Ali Alavi (University of Cambridge)
"Advances in Large scale CASSCF and Multi-reference Perturbation Theory using Full CI Quantum Monte"

ORIOLE ROOM 2
Complex Systems IB **Chair: J. Gao**
Xiaosong Li (University of Washington)
"Non-collinear Spin in Quantum Chemistry"

Irene Burghardt (Goethe University Frankfurt)
''High-dimensional Quantum Dynamics of Functional Organic Polymer Materials: Coherence and Correlations at the Nanoscale"

John Herbert (Ohio State University)
"*Symmetry-Adapted Perturbation Theory for Many-Body Systems"*

PHEASANT ROOM 3
DFT Subsystems IB **Chair: L. Visscher**
Weitao Yang (Duke University)
"Embedding of Two-Electron Subsystems within DFT for Ground and Excited States"

Piotr de Silva (Massachusetts Institute of Technology)
''Many-Pair Expansion: A Systematically Improvable Correction Scheme for Including Strong and Long-Range Correlations in DFT"

Kieron Burke (University of California-Irvine)
"A Foolish Consistency is the Hobgoblin of Little Minds"

2:00pm-3:30pm **AFTERNOON SESSION A**
BALLROOM 5
Molecular Properties IA **Chair: T. Helgaker**
Timo Fleig, (University of Paul Sabatier Toulouse)
"Atoms and Molecules as Laboratories for Probing Physics Beyond the Standard Model"

Peter Schmelcher, (University of Hamburg)
"Ultralong-Range Molecules: Binding, Properties and Control with External Fields"

Erik Tellgren, (University of Oslo)
"Non-perturbative Treatment of Molecules in Non-uniform Magnetic Fields"

ORIOLE ROOM 2
Complex Systems IIA **Chair: N. Ananth**
Donald Truhlar, (University of Minnesota)
"The Quest for a Universal Density Functional for Treating Complex Systems"

Neepa Maitra (Hunter College CUNY)
"Non-Adiabatic Dynamics in Strong Fields: Enhanced Ionization"

Robert Distasio (Cornell University)
"The Dipole Polarizability of a Condensed-Phase Water Molecule"

PHEASANT ROOM 3 **DFT Subsystems IIA** **Chair: ~~D. Crawford~~**

Adam Wasserman (Purdue University)
"Fixing Errors of Approximate XC-functionals with Partition Density Functional Theory"

Jason Goodpaster (University of Minnesota)
"Quantum Embedding Methods for Wave-Function-in-Density Functional Theory: Projection Based Embedding and Density Matrix Embedding Theory"

Mark Hoffmann (University of North Dakota)
"Chemical Bonds in Subsystem Embedding Theory with External Orbital Orthogonality"

3:30pm-4:00pm **Coffee Break** 

4:00pm-5:00pm **Plenary III** **Chair: K. Pernal**
BALLROOM 5
Kim Baldridge (Tianjin University and ETH Zürich)
"Structure–Property Relationships of Curved Aromatic Materials from First Principles"

5:00pm-6:30pm **AFTERNOON SESSION B**
BALLROOM 5 **Molecular Properties IB** **Chair: T. Fleig**

Filipp Furche, (University of California, Irvine)
"Unphysical Divergences in Approximate Response Theory"

Filip Pawlowski, (Aarhus University)
"Why Cluster Perturbation Theory and Not Coupled Cluster Theory?"

Andy Teale (University of Nottingham)
"Current-Density-Functional Theory: Progress and Challenges"

ORIOLE ROOM 2 **Complex Systems IIB** **Chair: N. Ananth**

Ryan Steele, (University of Utah)
"Vibrational Signatures of Electronic Properties in Energy and Biology"

Jiri Vanicek, (Ecole Polytechnique Federale de Lausanne)
"On-the-fly Ab Initio Semiclassical Dynamics for Computing Vibrationally Resolved Electronic Spectra"

Mark Tuckerman, (New York University)
"Exploration and Generation of Free Energy Landscapes of Molecular Crystals and Oligopeptides"

PHEASANT ROOM 3 **DFT Subsystems IIB** **Chair: C. Filippi**

Lyudmila Slipchenko, (Purdue University)
"BioEFP: Polarizable Embedding in Biological Systems"

Debashree Ghosh, (National Chemical Laboratory)
"Hybrid Quantum Mechanical / Effective Fragment Potential Methods: Towards Accurate Solvatochromic Shifts in Biological Medium"

Chen Huang (Florida State University)
"Patching Exchange-Correlation Potential in Density Functional Theory"

6:30pm-8:30pm **Poster Session I**
BALLROOM 4

TUESDAY, JULY 19

8:00am-9:30am **MORNING SESSION A**
BALLROOM 5 **Electronic Structure IIA** **Chair: H. Nakai**

Hans Lischka, (Tianjin University)
"The Polyradical Character of Kekulé and Non-Kekulé Structures of Polyaromatic Hydrocarbons"

Monika Musiał, (University of Silesia)
"Novel Treatment of the High-Multiplicity States with the EOM Method and RHF Reference Function"

Gustavo Scuseria, (Rice University)
"New Vistas on the Strong Correlation Problem"

ORIOLE ROOM 2 **DFT Subsystems IIIA** **Chair: G. Chan**

Thomas Miller, (California Institute of Technology)
"Quantum Embedding Methods for the Simulation of Condensed-Phase Systems"

Gang Lu, (California State University Northridge)
"Density-Based Embedding for QM/MM Modeling of Metals"

Johannes Neugebauer, (University of Muenster)
"Excited States in Protein-Pigment Complexes"

PHEASANT ROOM 3 **Chemical Insights IA** **Chair: T. Rocha-Rinza**

Pedro Salvador, (Universitat de Girona)
"One- and Two-Center Physical Space Decomposition of the Kohn-Sham Density Functional Theory Energy"

Carlos Cárdenas (University of Chile)
"Chemical Response Functions in Degenerate States and Extended Systems"

Laurent Joubert, (University of Rouen)
"Unraveling Charge Transfer Processes with the Quantum Theory of Atoms-in-Molecules"

9:30am-10:00am **Coffee Break** 

10:00am-11:00am **Plenary IV** **Chair: H. Nakatsuji**
BALLROOM 5 **Henry F. Schaefer III** (University of Georgia)

11:00am-12:30pm **MORNING SESSION B**
BALLROOM 5 **Electronic Structure IIB** **Chair: M. Kállay**

Ágnes Szabados, (Eötvös Loránd University)
"Novel Orthogonalization Algorithms and Their Use in Electronic Structure Theory"

Péter Surján, (Eötvös Loránd University)
"Convergence Enhancement in Rayleigh-Schrodinger Perturbation Theory: Quantum Chemical Applications"

Masahiro Ehara, (Institute for Molecular Science)
"Recent Progress in CAP/SAC-CI Method for Locating Resonance States"

ORIOLE ROOM 2 **DFT Subsystems IIIB** **Chair: M. Reiher**

Gerald Knizia, (Pennsylvania University)

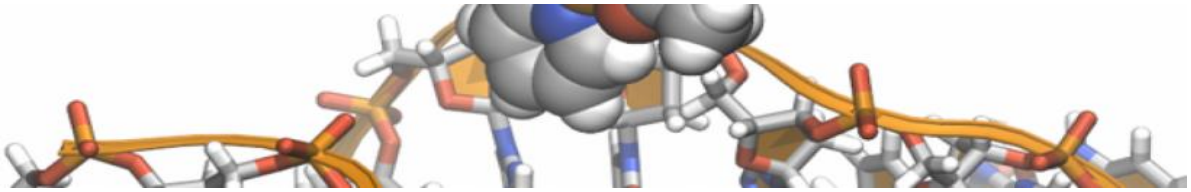
Andre Severo Pereira Gomes, (Laboratoire de Physique des Lasers Atomes et Molécules (PhLAM) CNRS)
"Frozen-density Embedding Calculation of Second-order Magnetic Properties in the Relativistic Framework"

Florian Libisch, (Vienna University of Technology)
"Embedding Approaches for Bulk Systems Using Projector-Augmented Waves"

PHEASANT ROOM 3 **Chemical Insights IB** **Chair: E. Matito**

Tomás Rocha-Rinza, (Universidad Nacional Autónoma de México)
"Some Developments of Quantum Chemical Topology and Their Applications to the Study of H-Bond In Ground and Excited States"

Ida-Marie Høyvik, (NTNU)



Frontiers in Computational Chemistry 2016

LA FACULTAD DE QUÍMICA Y EL INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

Otorgan la presente

C O N S T A N C I A

a:

Arturo Sauza de la Vega y Tomás Rocha Rinza

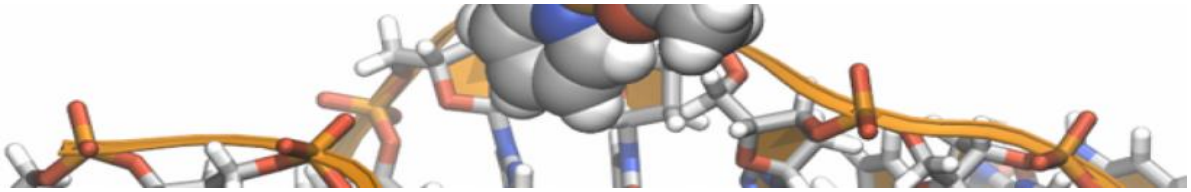
Por la presentación del trabajo
"Topology of the electron density and noncovalent interactions analysis in relevant dehydroalanines in medicinal chemistry"

Simposio "Frontiers in Computational Chemistry 2016"

Ciudad de México, 24 y 25 de agosto de 2016

Dr. Fernando Cortés Guzmán
Representante del Comité Organizador

FCC2016-SAIQ-0005



Frontiers in Computational Chemistry 2016

LA FACULTAD DE QUÍMICA Y EL INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

Otorgan la presente

C O N S T A N C I A

a:

Wilmer Esteban Vallejo Narváez

Por la presentación del trabajo
"A Combined Theoretical and Experimental Study of Amides and Imides Dimerization"

Simposio "Frontiers in Computational Chemistry 2016"

Ciudad de México, 24 y 25 de agosto de 2016

Dr. Fernando Cortés Guzmán
Representante del Comité Organizador

FCC2016-SAIQ-00057

El Comité Local y Nacional de la *XV* Reunión Mexicana de Fisicoquímica Teórica
otorga el presente

R E C O N O C I M I E N T O

a

Arturo Sauza, Tomás Rocha

por presentar el Cartel titulado:

Topología de la densidad electrónica y análisis de interacciones no covalentes en deshidroalaninas

dentro de la Reunión celebrada en la Cd. de Mérida, Yuc. México,
los días 17, 18 y 19 de Noviembre de 2016

Dr. Gabriel Merino
Representante del Comité Local y Nacional
de la XV Reunión Mexicana de Fisicoquímica Teórica

Cinvestav CONACYT intel LUFAC

El Comité Local y Nacional de la XV Reunión Mexicana de Fisicoquímica Teórica otorgan el presente

R E C O N O C I M I E N T O

a

Wilmer Vallejo, Tomás Rocha y Marcos Hernández

Por haber presentado el cartel:

Estudio teórico-experimental de las interacciones presentes en dímeros de amidas e imidas

Dentro de la reunión celebrada en la Cd. de Mérida, Yuc. México, los días 17, 18 y 19 de Noviembre de 2016.

Dr. Gabriel Merino
Representante del Comité Local y Nacional de la XV
Reunión Mexicana de Fisicoquímica Teórica

Cinvestav CONACYT intel LUFAC COMPUTACION S.A. de C.V.