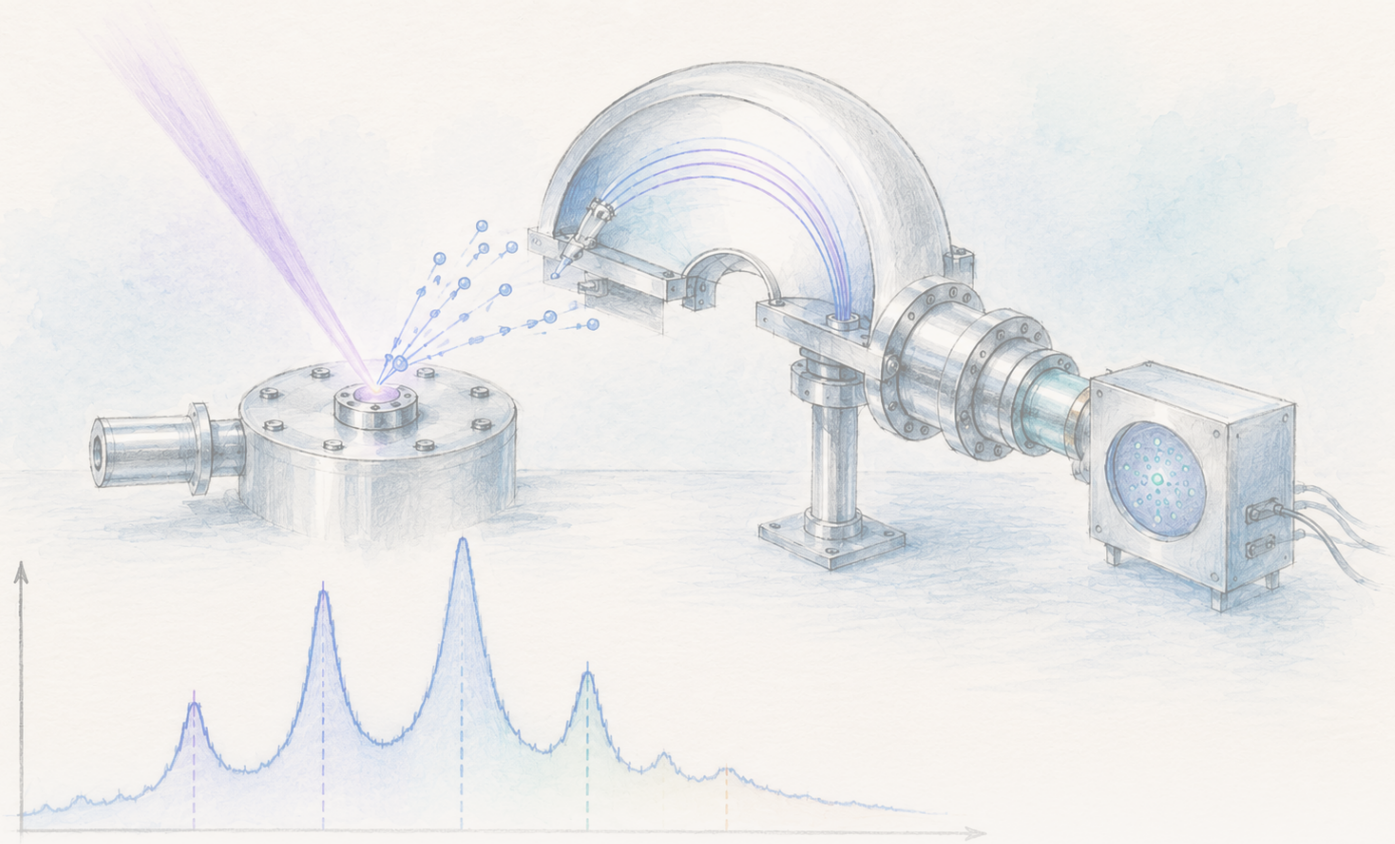


The Clean Paper

WHAT THE PAPER SAYS · WHAT IT DOESN'T · WHY IT MATTERS

Carbon–bismuth triple bond tana nuna inda textbook sigma-and-pi picture ke daina aiki

Wani Science study ya probe CBi^- molecular ion, heavy-element cousin na familiar triply bonded species, da cryogenic photoelectron spectroscopy da relativistic quantum calculations. Result direct evidence ne cewa strong spin-orbit coupling na iya reorganize classical sigma/pi framework zuwa relativistic Kramers pairs da total angular momentum. Wannan ba ya sa ordinary bonding wrong; yana nuna dalilin da bookkeeping ke canzawa kusa da very heavy atoms.

Written by Matteo · Cross-checked by Vera Rubin · Edited by Michele Renda · Figures by Nova Vela · AI-assisted, human-reviewed

Paper: *Relativistic collapse of the classical triple bond in the CBi- molecular ion*, Deniz Kahraman, Jie Hui, Xin-Yu Zhang, Neil A. Ellis, Hyun Wook Choi, Kirk A. Peterson and Lai-Sheng Wang, Science 393, 184-187 (2026) · DOI: 10.1126/science.aei1285

Yawanci ana iya zana haɗin atom uku cikin tsari mai sauƙi. Bismuth ya sa wannan sauƙin ya rushe

A tsarin da ake koyarwa a litattafai, **triple bond** ya ƙunshi haɗin sigma ɗaya da haɗin pi biyu. Haɗin **sigma** yana samuwa ne kai tsaye a layin da ya haɗa atom biyu, inda yawan electron ya fi taruwa. Haɗin **pi** kuwa yana samuwa ne a gefe: yawan electron yana sama da ƙasa, ko kewaye da wannan layi. Saboda haka, sigma ɗaya da pi biyu suna ba da hoto mai tsabta da sauƙin fahimta.

Wannan hoton ba wai sauƙaƙawa ce marar tushe ba. Ga atom masu sauƙin nauyi, sau da yawa yana aiki sosai saboda ana iya bayyana electrons da orbitals waɗanda siffarsu da spin ɗinsu za a iya ɗauka daban-daban a tunani.

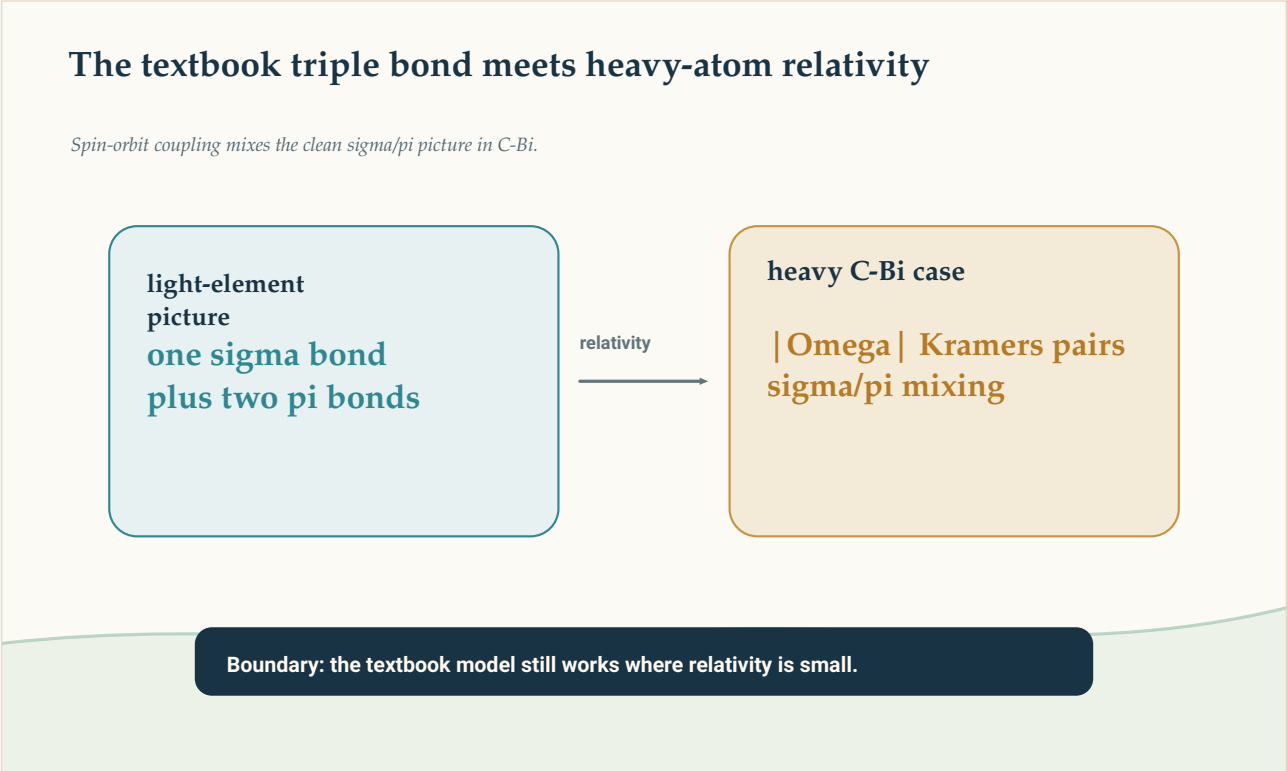
Don haka hoton ba ƙarya ba ne. Kyakkyawan kusanci ne ga yawancin misalan da ake gani a litattafan chemistry.

Amma bismuth ba ya cikin wannan yanayi mai sauƙi.

Bismuth yana da protons 83. Kusa da nucleus mai nauyi haka, tasirin relativity ba ƙaramin gyara ba ne da za a iya ƙara daga baya; yana zama wani ɓangare na chemistry kanta. Electrons suna motsi a cikin field mai ƙarfi har **spin-orbit coupling** — haɗin tsakanin spin na electron da motsinsa a orbital — zai iya zama ɗaya daga cikin abubuwan da suka fi tsara halayen tsarin. Idan haka ta faru, tsoffin sunaye ba sa daina aiki saboda an manta da su; suna daina zama hanyar da ta fi dacewa wajen bayyana abin da ke faruwa.

Sabuwar takarda a *Science* daga Deniz Kahraman, Jie Hui, Xin-Yu Zhang, Neil A. Ellis, Hyun Wook Choi, Kirk A. Peterson da Lai-Sheng Wang ta binciki wani misali da aka zaɓa da gangan domin ya fito da wannan matsala fili: ion ɗin carbon-bismuth **CBi^-**. Yana da adadin valence electrons iri ɗaya da CN^-, wanda sanannen misali ne na triple bond tsakanin atom masu sauƙin nauyi. Amma maye gurbin nitrogen da bismuth yana ɗaukar irin wannan matsalar ƙidayar electrons zuwa yanayin da tasirin relativity ya fi ƙarfi sosai.

Sakamakon ba wai “triple bonds ba daidai ba ne” ba. Ya fi takamaimai, kuma ya fi ban sha’awa: a CBi^-, bayanin gargajiya na sigma ɗaya da pi biyu ya daina wadatarwa, kuma sai a koma ga bayanin relativistic da aka gina da **Kramers pairs**, waɗanda ake warewa da projection na jimillar angular momentum. Haɗin atom ɗin yana nan. Abin da ya gaza shi ne tsohuwar hanyar rarraba shi.



A triple bond tsakanin atom masu sauƙin nauyi ana iya bayyana shi da sigma ɗaya da pi biyu. A C–Bi mai nauyi, spin-orbit coupling yana sake tsara wannan zuwa Kramers pairs na |Ω| waɗanda sigma da pi suka gauraya. Haɗin yana nan — tsoffin sunayen litattafi ne suka daina wadatarwa.

Original diagram — The Clean Paper CC BY 4.0

Abin da marubutan suka auna

Marubutan sun samar da CBi^- a cikin molecular beam ta hanyar laser ablation na wani target mai bismuth da graphite, sannan suka binciki anion ɗin da high-resolution cryogenic photoelectron spectroscopy da photoelectron imaging. **Anion** ion ne mai cajin lantarki mara kyau; a nan CBi^- shi ne molecule na carbon da bismuth da ya samu ƙarin electron guda ɗaya.

Photoelectron spectroscopy tana yin wani abu mai sauƙin bayani amma mai wahalar aiwatarwa. Photon yana fitar da electron daga anion. Idan aka auna electron ɗin da ya fita, za a iya sanin adadin energy da aka buƙata, sannan a gano wane electronic state na molecule mara caji aka kai. Wannan neutral electronic state yana nufin ɗaya daga cikin tsarin da sauran electrons za su iya ɗauka bayan an cire ƙarin electron ɗin. Photoelectron imaging kuma tana ƙara bayanin alkiblar electrons ɗin da suka fita; wannan tsari yana taimakawa wajen gano irin orbital ɗin da electron ya fito daga gare shi.

[video pending]

Wani ɗan gajeren bidiyon koyarwa ne game da photoemission: haske mai shigowa yana fitar da electrons daga abu, sannan energy ɗinsu tana bayyana states da aka bari a baya. Wannan shi ne ka'idar da photoelectron

spectroscopy ta wannan binciken ta dogara da ita, amma bidiyon ba gwajin CBi^- kansa ba ne. The Clean Paper ta mayar da shi zuwa MP4 domin ya dace da browser; ba a canza abin da bidiyon ya ƙunsa ba.

Babban spectrum da aka ɗauka a 4.661 eV ya nuna electronic bands uku, waɗanda aka sa wa suna X, A da B. A molecular spectroscopy, X yawanci yana nuna ground electronic state — state mafi ƙarancin energy na neutral molecule — yayin da A da B suke nuna states masu energy mafi girma da suka bayyana a spectrum. Wani spectrum da aka ɗauka da energy mafi girma, 6.424 eV, bai nuna ƙarin features ba.

Ma'aunin high-resolution ya ba da adiabatic detachment energies kamar haka:

- **2.3429 eV** ga state X, wanda shi ne electron affinity na neutral CBi;
- **2.5812 eV** ga A;
- **3.5246 eV** ga B.

Rashin tabbas da marubutan suka bayar yana kusan **0.0010 eV** ga electronic energies da **8 cm^{-1}** ga vibrational frequencies.

Vibrational frequencies da aka auna su ne:

- X: **681 cm^{-1}**;
- A: **606 cm^{-1}**;
- B: **633 cm^{-1}**.

Waɗannan lambobin suna ba da bayani game da irin bonding a kowane neutral state. A matsayin kusanci na farko, bond mai gajarta kuma mai ƙarfi yakan ba da stretching frequency mafi girma; bond mai rauni ko mai tsawo yakan rage ta. Ba ƙa'ida ce marar ƙyale banbanci ba, amma hanya ce mai amfani ta fara fahimtar sakamakon.

Inda tsohon hoton ya fara kasa

Idan ba a yi la'akari da relativity ba, za a iya kallon CBi^- kamar nau'in CN^- mai bismuth: sigma orbital ɗaya cike da electrons, tare da pi orbitals biyu cike. Idan aka cire electron guda ɗaya, ana sa ran samun neutral states da za a iya warewa da harshen sigma da pi na yau da kullum.

Amma ma'aunin bai bi wannan tsari mai sauƙi ba.

Matsala ta farko ta fito ne daga yadda electrons suka watse zuwa alkibla daban-daban. Detector ɗin ba energy kaɗai yake aunawa ba; yana kuma auna alkiblar da electrons suka tashi. Ana taƙaita wannan tsarin da wani **anisotropy parameter beta**. Ga band X, beta ya kai **1.86**, wanda marubutan suka fassara a matsayin p-wave detachment da ya fi fitowa daga orbital mai halin sigma. Ga A da B kuma beta ya kasance **−0.73** da **−0.67**, abin da ya fi dacewa da detachment mai halin pi.

Har zuwa nan, za a iya cewa X ya fi kama da sigma, A da B kuma sun fi kama da pi.

Sai dai vibrational structure bai yarda da wannan rarrabawar mai sauƙi ba. Bayan an cire electron, molecule na iya kasancewa yana vibration; jerin peaks da wannan ke haifarwa ana kiransa **Franck–Condon progression**. X da B suna da gajerun progressions masu kama da juna, yayin da A ke da doguwa. Idan A da B kawai su ne spin-orbit

components biyu na ordinary pi-hole state guda ɗaya, ya kamata canjin bond length ɗinsu ya fi kama da juna. Maimakon haka, B yana kama da X ta wata fuska, kuma yana kama da A ta wata.

Irin wannan sabani yana da sauƙin ɓoyewa a ƙarƙashin zane mai kyau. Marubutan sun yi akasin haka: sun ɗauke shi a matsayin alamar cewa zane na tsohon model ba shi ne hanyar da ta dace da wannan molecule ba.

Bayanin relativistic

Ga atom masu nauyi, ba za a iya ware spin da orbital motion cikin sauƙi ba. Quantity da ya fi kasancewa conserved shi ne projection na **jimillar electronic angular momentum** a kan molecular axis. Takardar ta nuna wannan da Ω (**omega**).

Wannan yana sauya tushen bayanin. Maimakon a ɗauki triple bond a matsayin sigma ɗaya da pi biyu sannan a ƙara spin daga baya, marubutan suna bayyana states ɗin da **relativistic Kramers pairs**. Kramers pair wasu spinors biyu ne masu energy iri ɗaya waɗanda time-reversal symmetry ke buƙata a tsarin da ke da odd number na electrons. Kalmar tana da fasaha, amma muhimmin ra'ayi mai sauƙi ne: a yanayin relativistic, abubuwan one-electron da suka fi dacewa su ne **spinors**, ba orbitals marasa spin da za a manna musu spin daga baya ba.

Fully relativistic calculation ɗin ya ba da Kramers pair ɗaya mai kusan halin pi tsantsa, **|Ω| = 3/2**, da wasu pairs biyu na **|Ω| = 1/2** waɗanda sigma da pi suka gauraya sosai. A sauƙaƙe, pair ɗaya har yanzu ya fi kama da pi, amma sauran biyun ba za a iya ware su a sarari a matsayin sigma ko pi ba. Wannan shi ne "collapse" da taken takardar yake nufi: ba bond ɗin ne ya ɓace ba; rarrabawar gargajiya tsakanin sigma da pi ce ta daina zama harshen da ya fi dacewa da wannan molecule.

Lissafin theory ba ƙarin ado ba ne da aka kawo bayan gwaji. Marubutan sun yi amfani da four-component Dirac–Coulomb coupled-cluster methods, ciki har da DC-CCSD(T) ga ground state da low-lying states, da EOM-IP-CCSD ga state B. Bond length na C–Bi da aka lissafo ga CBi^- ya kai **2.022 Å**, yayin da stretching frequency na anion da aka lissafo ya kai **695 cm^{-1}**, kusa da ma'aunin gwaji. Adiabatic detachment energies da lissafin ya bayar sun yi daidai sosai da X da A da aka auna, kuma suna goyon bayan relativistic assignment.

State B shi ne ɓangaren da ya fi wahala a lissafin. Vibrational frequency da aka lissafo masa bai yi daidai da gwaji sosai ba. Marubutan suna ganin wannan alama ce cewa frequency ɗin tana da matuƙar saurin sauyawa gwargwadon yadda states X da B suka gauraya. Wannan ƙaƙƙarfan mixing na |Ω| = 1/2 shi ne kuma abin da ke sa frequency na B ya fi na A sosai. Bayanin bincike bai kamata ya sa sakamakon ya zama mafi tsabta fiye da yadda takardar kanta ta nuna ba.

Abin da wannan binciken bai tabbatar ba

- Ba yana nufin harshen sigma da pi na yau da kullum ya zama mara amfani ba.
- Ba yana nufin sai an sake zana C–N triple bonds, alkynes ko yawancin misalan atom masu sauƙin nauyi a litattafai ba.
- Bai tabbatar cewa kowane bond da ke ɗauke da heavy element yana yin irin na CBi^- ba.
- Ba ya cewa C–Bi ba multiple bond ba ne.

- Ba ya mai da relativistic quantum chemistry wani ƙarin ado da za a iya barin sa; a wannan yanayin ana buƙatarta domin a samu assignment da ya dace.
- Ba ya ƙirƙirar sabon material ko sabuwar fasahar chemistry da kansa.

Muhimmin abu shi ne iyakar inda tsohon bayani yake aiki. Harshen classical bonding yana aiki sosai idan assumptions ɗinsa suna kusan cika. CBi^- yana da amfani saboda a nan an matsa waɗannan assumptions har gazawarsu ta zama abin da za a iya gani a gwaji.

Yaya ƙarfin shaidar yake?

Shaidar tana da ƙarfi wajen goyon bayan assignment ɗin da marubutan suka yi.

A bangaren gwaji, takardar ta haɗa high-resolution cryogenic spectra, vibrational structure da photoelectron angular distributions. Waɗannan hanyoyi suna takaita yiwuwar bayani ta hanyoyi daban-daban: tazarar energies kaɗai ba za ta isa haka ba; angular distributions kaɗai ma ba za su isa ba. Sabani da haɗin bayanan biyu ne suka nuna bukatar relativistic interpretation.

A bangaren lissafi, marubutan sun yi amfani da fully relativistic four-component methods maimakon su fara da nonrelativistic calculation sannan su ƙara spin-orbit coupling a matsayin ƙaramin correction. Wannan yana da muhimmanci domin ainihin ikirarin shi ne spin-orbit coupling **ba ƙarami ba ne** a wannan molecule.

Daidaiton bai zama cikakke ba. Vibrational frequency na state B shi ne babban abin da bai rufe sosai ba. Haka kuma takardar molecule ion guda ɗaya ce ta bincika, ba dukkan chemistry na heavy elements ba. Amma a matsayin benchmark ga relativistic bonding, CBi^- misali ne mai kyau sosai: molecule ce ƙarama, gwaji ya iya warware states ɗinta, kuma theory na iya lissafa ta da cikakken bayani.

Me ya sa wannan yake da muhimmanci

Sau da yawa chemistry tana koyar da bonding ta hanyar hotuna. Wannan ba rauni ba ne. Hoto mai kyau yana taƙaita quantum mechanics zuwa wani tsari da mutum zai iya amfani da shi.

Amma kowane hoto yana da iyakar inda yake aiki. Hoton triple bond na sigma/pi ya dace da yanayin da spin-orbit coupling ba shi ne babban abin da ke tsara tsarin ba. Heavy elements na iya fita daga wannan yanayin. CBi^- yana nuna wannan sauyin a molecule mai ƙaramin girma har za a iya auna gazawar tsohon hoton da lissafa ta daki-daki.

Wannan yana da muhimmanci ga chemistry na heavy elements domin bismuth da makwabtansa a periodic table ba wasu abubuwa ne da tasirin relativity ya shafe su kawai a yanayi na musamman ba. A wajensu, relativity wani ɓangare ne na yadda ake lissafin chemistry ta yau da kullum. Idan chemists suna son tsarawa, fassara ko hasashen bonding kusa da heavy atoms, suna buƙatar harshen da ke kiyaye quantities da suka dace.

Darajar wannan takarda ba wai ta sa tsohon hoto ya zama abin dariya ba ne. Ta yi wani abu mafi amfani: ta nuna daidai **inda** tsohon hoton ya fara kasa ɗaukar nauyin bayanin.

Taƙaitaccen bayani

Kahraman, Hui, Zhang, Ellis, Choi, Peterson da Wang sun auna ion ɗin CBi^- da high-resolution cryogenic photoelectron spectroscopy da photoelectron imaging, sannan suka kwatanta spectra ɗin da fully relativistic Dirac–Coulomb coupled-cluster calculations. Sun gano neutral states uku na CBi da adiabatic detachment energies **2.3429, 2.5812 da 3.5246 eV**. Spectra da angular distributions ɗin ba su dace da sauƙaƙƙen hoton nonrelativistic na sigma ɗaya da pi biyu ba. Maimakon haka, spin-orbit coupling mai ƙarfi yana sake tsara bonding ɗin zuwa relativistic Kramers pairs: pair ɗaya mai halin pi na **|Ω| = 3/2**, da pairs biyu na **|Ω| = 1/2** da sigma/pi mixing. Wannan shaida ce kai tsaye cewa a triple-bond system da ke ɗauke da heavy element sosai, tsoffin orbital labels na litattafai ba su ne mafi dacewar quantities da za a yi amfani da su ba. Ba ƙin amincewa da ordinary chemical bonding ba ne; taswira ce mai kyau da ke nuna inda relativity ta fara karɓar aikin bayanin.

Majiyoyi

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